



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/16826 <b>(22) International Filing Date:</b> 24 September 1997 (24.09.97) <b>(30) Priority Data:</b> 08/719,543                      25 September 1996 (25.09.96)    US 08/719,622                      25 September 1996 (25.09.96)    US <b>(71) Applicant (for all designated States except US):</b> CONTINENTAL PET TECHNOLOGIES, INC. [US/US]; Suite 490, 7310 Turfway Road, Florence, KY 41042 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SCHMIDT, Steven, L. [US/US]; 39 McIntosh Lane, Bedford, NH 03110 (US). AGRAWAL, Amit, S. [IN/US]; 141 London Court, Merrimack, NH 03054 (US). COLEMAN, Ernest, A. [US/US]; 293 Janes Lane, Stamford, CT 06903 (US). <b>(74) Agent:</b> HENDRICKS, Therese, A.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> TRANSPARENT OXYGEN-SCAVENGING ARTICLE INCLUDING BIAXIALLY-ORIENTED POLYESTER <b>(57) Abstract</b> <p>A transparent oxygen-scavenging article for packaging oxygen-sensitive products, such as beer, juice, ketchup, etc. The oxygen-scavenging article includes a biaxially-oriented aromatic polyester polymers such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN), and an oxygen-scavenging aromatic ester polymer compatible with the polyester polymer. The oxygen-scavenging polymer includes aromatic groups and alpha-hydrogen carbonyl groups of formula (I). Examples are polyesters from succinic, glutaric, adipic or suberic acid with hydroquinone, bisphenol A, styrene oxide or distyrene glycol or an aliphatic dicarboxylic acid containing copolyethylene naphthalate. Both polymers could form a copolymer, a blend or preferably different layers of the article. The oxygen-scavenging polymer may be incorporated into a barrier package at a competitive price, and provide the desired properties of transparency, thermal resistance, and pressurized strength.</p> <div style="text-align: right; margin-right: 100px;"> <math display="block">\text{---O---}\overset{\text{O}}{\underset{\text{  }}{\text{C}}}\text{---}(\text{CH}_2)_n\text{---} \quad (I)</math> </div>		

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## TRANSPARENT OXYGEN-SCAVENGING ARTICLE INCLUDING BIAXIALLY-ORIENTED POLYESTER

### Field of the Invention

5                   The present invention is directed to oxygen-scavenging materials and packages for holding oxygen-sensitive products, and more particularly to a transparent article incorporating an oxygen-scavenging aromatic ester polymer and a biaxially-oriented polyester, the article being useful for protecting oxygen-sensitive products from deterioration.

### 10   Background of the Invention

                  Plastic packaging has certain inherent benefits over glass and metal packaging, such as light weighting, variability in package design, non-breakability, and reduced cost of manufacture. However, plastic packaging may have greater permeability to certain gases (oxygen and carbon dioxide) and liquids (water) than glass or metal; these gases/liquids permeate  
15   through the plastic and reduce the shelf life of the product contained therein. Various specialty plastics and layer structures have been developed to provide commercially-acceptable plastic barrier packages with an acceptable shelf life for certain oxygen-sensitive products, such as juice and ketchup.

                  There are two general types of oxygen-barrier materials -- passive and active. A  
20   "passive" barrier prevents oxygen permeation into the package. For example, with multilayer technology it is possible to incorporate thin layers of expensive barrier polymers (e.g., polyvinylidene chloride copolymer (PVDC) or ethylene vinyl alcohol copolymer (EVOH)), or thin layers of metal films, in combination with structural layers of commercially-available plastic resins, e.g., polyethylene terephthalate (PET).

25                   In an "active" barrier system, an oxygen "scavenger" is incorporated into a single or multilayer plastic structure to consume the oxygen initially present and/or generated from the inside of the package, as well as to prevent exterior oxygen from reaching the interior of the package. Thus, oxygen scavengers both remove oxygen from inside the package and prevent its ingress into the package.

30                   Another important design parameter for oxygen-barrier packaging is thermal resistance. Often the product must be "sterilized" in a process which exposes the package to high temperatures and/or pressures. For example, in a commercial "hot-fill" process, the product (e.g., juice) is at a temperature of 80-85°C when introduced into the container, the container is

then sealed (capped), and the juice/container allowed to cool. The container must withstand both the hot-filling temperature and the vacuum generated in the sealed container as the product cools, without distortion. Commercially successful hot-fill juice containers have been developed by Continental PET Technologies, Inc. of Bedford, New Hampshire, which provide a 1.5 to 4-time  
5 improvement in oxygen barrier property over a standard commercial single-layer PET container. These multilayer juice containers include two very thin intermediate barrier layers of EVOH positioned between inner and outer layers of virgin PET, and a core layer of either virgin or recycled PET.

However, there are products which are even more "oxygen sensitive" than juice.  
10 For example, most beers require at least 10 times greater oxygen barrier protection than provided by a standard commercial single-layer PET container. In addition, most beer is packaged by a "wet pasteurization" process in which the beer is introduced to the container at a temperature of about -1 to 7°C, the container is sealed, and the sealed container is then immersed in a 60-75°C bath for at least 10 minutes (see Fig. 12). This pasteurization process may be considered even  
15 more degrading than hot-filling in that the container is exposed to an elevated temperature for a much longer period of time. Also, beer is carbonated and thus the sealed container must hold a pressurized liquid during this extended high-temperature immersion. Both the increased temperature and pressure produce expansion forces on the container sidewall, which forces may delaminate the layers in a multilayer container.

20 Yet another problem that must be overcome for packaging beer in plastic containers is carbon dioxide (CO<sub>2</sub>) permeation. To maintain shelf life, the container must provide a CO<sub>2</sub> barrier which minimizes the amount of CO<sub>2</sub> leaving the beer over the designated shelf life.

The beer bottling companies presently have billions of dollars invested in wet  
25 pasteurization equipment and therefore are unlikely to adopt a new package unless it can withstand this process. A standard commercial single-layer PET container can not survive the wet pasteurization process, nor provide the necessary barrier properties. Known multilayer PET/EVOH containers also cannot provide the necessary barrier properties for beer, at a competitive price.

30 Attempts have been made to provide a single or multilayer container including polyethylene naphthalate (PEN), a polyester similar to polyethylene terephthalate (PET), but having a substantially increased oxygen-barrier property and increased thermal resistance.

However, the cost of PEN is significantly greater than PET such that no cost-effective alternative has yet found wide-spread acceptance.

Furthermore, the materials used must be approved by governmental authorities, e.g., the U.S. Food and Drug Administration, for the packaging of food products. All of these factors, coupled with the greater expense (of raw materials and cost of processing) of the known oxygen-scavenging polymers, have prevented the commercial acceptance of a plastic barrier package for beer.

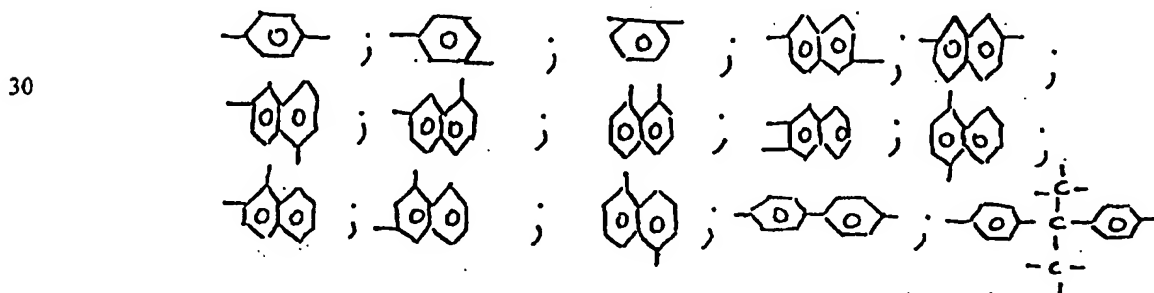
Thus, in spite of a long-recognized need and large size of the potential market, there is an on-going need for improvements in plastic barrier packaging which can withstand the stringent thermal, pressure and gas permeability requirements for a plastic beer container.

### Summary of the Invention

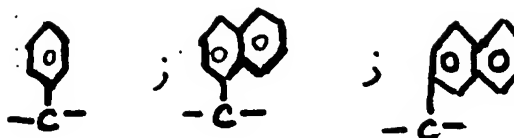
The present invention is directed to a transparent oxygen-scavenging article, which includes a biaxially-oriented aromatic polyester polymer and an aromatic ester scavenging 15 polymer. The scavenging polymer has alpha-hydrogen carbonyl groups:



where  $n = 2$  or more, which provide the oxygen-scavenging function. The relative weight percentages of the alpha-hydrogen carbonyl groups and aromatic groups are selected to provide a desired rate of oxygen scavenging and a  $T_G$  which allows biaxial orientation of the polyester polymer without substantial loss of transparency. The aromatic groups provide single or multiple aromatic rings in the backbone or sidechain of the scavenging polymer, and preferably include, in the backbone:



and in the side chain:



5           The article may be a film or package, or a portion thereof; examples include a film stretched in transverse directions and a blow-molded container which has undergone axial and hoop expansion. The article may be a single layer or multiple layers. The scavenging polymer may be provided in a separate layer from the polyester, or it may be blended with or copolymerized with the polyester.

10           The object of the present invention is to provide a scavenging polymer which is compatible with aromatic polyesters such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), such that the polyester can be biaxially-oriented without loss of transparency. Transparency may be defined as the percent haze for transmitted light through the article wall or film thickness  $H_T$  (as hereinafter defined), measured in accordance with ASTM  
15   Method D1003 using a standard color difference meter. The article preferably has a percent haze of less than 10 percent, and more preferably less than 5 percent.

          The process compatibility of the scavenging polymer and polyester is indicated by the glass transition temperatures ( $T_G$ ) of the two polymers, whereby either a blend, copolymer, or separate layers of the polymers can be processed in the same temperature range without loss of  
20   transparency, i.e., held at a temperature above  $T_G$  and stretched in transverse directions to biaxially orient the polyester. Preferably, the average biaxial stretch ratio is from 9:1 to 15:1. The  $T_G$  of the scavenging polyester may be adjusted by varying the percentage of aromatic groups in the polymer -- with increasing amounts of aromaticity increasing the  $T_G$ .

          Generally, the  $T_G$  of a polymer used in a commercial plastic container must be at  
25   least 5°C above the ambient use temperature, e.g., if a carbonated beverage bottle will be used in an environment where the temperature may reach 35°C, the polymer should have a  $T_G$  of at least 40°C or the polymer may melt (no longer be a solid article). The  $T_G$  also determines the temperature above which an aromatic polyester must be heated to enable biaxial stretching, which orients and partially crystallizes the polymer to provide structural strength. For example,  
30   PET has a  $T_G$  of about 70°C, and PEN has a  $T_G$  of about 120°C; for ease of processing, the polymers are typically stretched in an orientation temperature range of at least 20°C above  $T_G$  (e.g., at least 90°C for PET, at least 140°C for PEN, and varying with the copolymer content). It

is desirable for the scavenging polymer to have a  $T_G$  below the orientation temperature of the polyester which is to be biaxially oriented (e.g., PET or PEN), but not so far below that the scavenging polymer will crystallize (become nontransparent or opaque) during the orientation process. The  $T_G$  of the scavenging polymer should be at least 10°C below the orientation  
5 temperature used to biaxially orient the polyester. A preferred range of  $T_G$  for a scavenging polymer having an amorphous nature (i.e., not crystallizing more than 3% under any conditions), is 0-15°C below the  $T_G$  of the polyester, more preferably 3-7°C below, and most preferably about 5°C below. A preferred range of  $T_G$  for a crystallizable scavenging polymer is 0-15°C above the  $T_G$  of the polyester, more preferably 3-7°C above, and most preferably about 5°C above.

10 Thus, in order to remain a solid article under generally accepted commercial use conditions, the scavenging polymer should have a  $T_G$  of at least 40°C, preferably at least 48°C, and more preferably in the range of 70-135°C. For ease of processing with PET polymers, the scavenging polymer preferably has a  $T_G$  of 70-85°C, and for ease of processing with PEN polymers a  $T_G$  of 120-135°C. For amorphous scavengers, a lower  $T_G$  of 90-100°C for use with  
15 PEN polymers is acceptable.

In general, the relative molar or weight percentages of the various groups in the scavenging polymer are selected to optimize the desired scavenging and compatibility characteristics. Thus, increasing the alpha-hydrogen carbonyl groups will increase the oxygen-scavenging rate. The ester groups (COO) provide compatibility with the polyester. Increasing  
20 the aromatic groups increases the  $T_G$ . Increasing the aliphatic chain length (adjacent to the carboxy group) may increase the oxygen-scavenging capacity (scavenging performance over the shelf life of the container) as described below.

Without wishing to be limited to any theoretical explanations, it is believed that the oxygen-scavenging properties of these polymers result from the presence of the carbonyl  
25 groups which provide a non-uniformity, such as a kink, in the backbone molecular structure at or near the location of the carbonyl group. It is believed that this non-uniformity decreases the chemical stability of the hydrogen atoms bonded to the atoms alpha to the carbonyl carbon. As a result, these hydrogen atoms have a significantly reduced bond strength which is then much more easily disassociated by diatomic gaseous oxygen, and thus have a relatively high propensity to  
30 react with oxygen, resulting in the oxygen-scavenging property.

This is in contrast to prior known oxygen-reactive materials that utilize carbon-carbon double bonds (unsaturation) in the backbone of the polymer to provide oxygen reactivity.

As a result, the oxygen-scavenging polymers of the present invention need not include any carbon-carbon double bonds in the backbone to achieve scavenging.

The aliphatic chain (e.g.,  $(CH_2)_n$ ) adjacent the carbonyl carbon is believed to provide continuing (cascading) sites for oxygen consumption, as illustrated in the steps of Figs.

5 13A-13K.

In Fig. 13A, we start with an ester group having a 2-carbon aliphatic chain attached to the carbonyl, and an oxygen molecule ( $O=O$ ) approaches (to be consumed).

In Fig. 13B, the oxygen molecule has liberated an alpha hydrogen to form a radical on the alpha carbon and radicalize the oxygen molecule as:  $\cdot O-O-H$ .

10 In Fig. 13C, the radical of the alpha carbon is satisfied, at least temporarily, by attachment of the radical  $\cdot O-O-H$ . Another oxygen molecule is added to further the reaction and eventually be consumed.

In Fig. 13D, the free oxygen molecule liberates a second alpha hydrogen, producing a new radical on the first alpha carbon and again forming a free  $O-O-H$  radical.

15 In Fig. 13E, three reactions occur simultaneously:

1. The H on the free radical  $\cdot O-O-H$  combines with the  $-O-H$  at the end of the  $-O-O-H$  attached to the alpha carbon, to produce water (circled in Fig. 13E).
2. When the water is produced, the previous free radical  $\cdot O-O-H$  becomes  
20 simple oxygen  $O=O$ .
3. The radical on the alpha carbon shifts to the attached oxygen atom to form a double bond (shown by arrow).

In Fig. 13F, the final stable reactants are shown. The new carbonyl is in the position of the previous alpha hydrogen, a water molecule is formed, and an oxygen molecule is  
25 now free.

In Fig. 13G, either the free oxygen molecule  $O=O$ , or any other available oxygen molecule, liberates an alpha hydrogen from the newly formed (second) alpha carbon, producing a radical on the second alpha carbon and a free radicalized oxygen molecule  $\cdot O-O-H$ .

30 In Fig. 13H, the radicalized oxygen molecule  $\cdot O-O-H$  attaches itself to the second alpha carbon temporarily satisfying the radicals. Another oxygen molecule is added to be consumed. The water molecule resulting from the previous steps is not shown for it is no longer involved in any reactivity.



In Fig. 13I, the newly arrived oxygen molecule,  $O=O$ , liberates the remaining alpha hydrogen to produce a free radicalized  $\cdot O-O-H$  and form a radical on the second alpha carbon.

In Fig. 13J, again there is a multi-step reaction, like that shown in Fig. 13E, where  
5 the  $-O-H$  from the  $-O-O-H$  attached to the second alpha carbon, liberates the hydrogen of the free radical  $\cdot O-O-H$  to produce water. This again produces an oxygen molecule,  $O=O$ . The remaining radical of the second alpha carbon moves to the remaining attached oxygen atom to form a double bond to the oxygen.

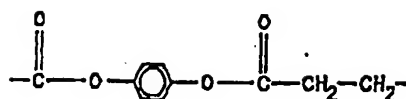
In Fig. 13K, the final form of the molecular structure is shown with all the alpha  
10 hydrogens liberated to produce water, and all the alpha carbons have become carbonyls. Also shown is the recently de-radicalized oxygen molecule coming from the  $\cdot O-O-H$  radical. This illustrates the continuing (cascading) scavenging function of the aliphatic chain, wherein the larger the chain the greater the number of potential scavenging sites. It is understood that this extends the scavenging potential over time, i.e., extends the shelf life of the package.

15 Compatibility of the scavenging polymer and polyester is generally indicated by a substantial match of solubility parameters. For example, the Van Krevelen solubility parameters (as hereinafter defined) for the scavenging polymer and the polyester are preferably within 3 units and more preferably within 1 unit. The solubility match enhances blending and adhesion of the polymers.

20 The compatibility of the scavenging polymer and polyester may be further indicated by crystallization rate, with the crystallization rate of the scavenging polymer less than or equal to that of the polyester. This provides process compatibility to enable biaxial orientation of the PET, in either a blend, copolymer or a separate layer, without loss of transparency.

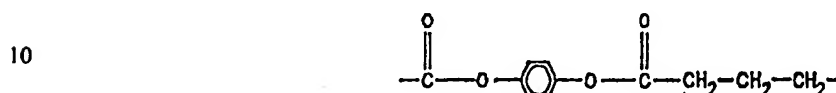
The aromatic ester scavenging polymer may be a homopolymer, a random  
25 copolymer, an alternating copolymer, or a block copolymer. The scavenging polymer must include alpha-hydrogen carbonyl groups to provide the oxygen-scavenging functionality, and aromatic and ester groups for compatibility with the polyester. The polymer may include other functional groups, so long as the compatibility with the polyester is maintained.

For example, a preferred scavenging homopolymer has the single-repeating unit  
30 set forth below and is referred to as REVPET:



The REVPET repeating unit has the same amount of aromaticity (a single backbone ring) and number of ester groups (two) as PET, and the same 2-carbon (ethyl) group in the backbone. It provides an exact match of solubility parameter.

An alternative homopolymer has the single-repeating unit defined below, and is referred to as Modified REVPET:



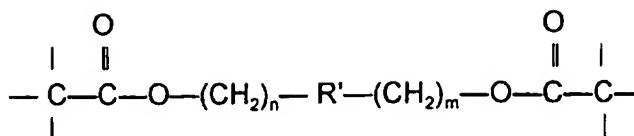
Modified REVPET has a very close match of solubility parameter. There is an extra carbon atom in the aliphatic carbon chain which reduces the  $T_g$ . Depending on the application, it may be desirable to form a copolymer (e.g., add additional groups which modify  $T_g$  or the crystallization rate). Various other scavenging polymers are described in the detailed description.

A preferred transparent oxygen-scavenging article is a multilayer package, such as a blow-molded container, having one or more layers of a biaxially-oriented PET polymer and one or more layers of a scavenging polymer such as REVPET. The thickness of the REVPET layer(s) may range from relatively thin (e.g., about 2% by weight of the container) to relatively thick (e.g., about 40% by weight of the container).

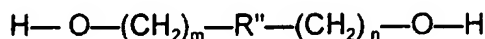
In one embodiment, an aromatic ester scavenging condensation polymer may be prepared from a dicarboxylic aliphatic acid having the formula:



where  $n = 2$  or more, and preferably 2-10, or a derivative of the acid (e.g., dimethyl ester, acid chlorides, acid anhydrides, diacyl chlorides), to provide the alpha-hydrogen carbonyl groups. The dicarboxylic aliphatic acid (or derivative) is reacted with one or more aromatic glycols or diacetates, having the general formula:



or



- 10 where n and m are the same or different integers from 0 to 6, and R' and R'' are the same or different previously described aromatic backbone or side chain groups (see pages 4-5). These glycols and diacetates provide the aromatic rings and adjacent oxygens (the backbone oxygen in the ester group of the aromatic ester polymer). Preferably, the molar ratio of aromatic groups : ester groups : alpha hydrogen carbonyl groups is 1:2:2 for polycondensation homopolymers.
- 15 Copolymers often have different ratios to optimize the T<sub>g</sub> of the scavenging polymer.

It is expected that cobalt will enhance the oxygen-scavenging rate of the aromatic ester scavenging polymers of this invention. Preferably, 50-500 micrograms of cobalt is added per gram of scavenging polymer. Preferably, the cobalt is added in the form of cobalt neodecanoate or cobalt acetate. Alternative enhancers include magnesium and manganese

20 acetates.

These and other features of the present invention will be more particularly described in the following detailed description and drawings.

#### Brief Description of the Figures

- 25 Figs. 1A-1K show methods for making various polymers including a prior art two-step method for preparing PET (Fig. 1A), and in Figs. 1B-1K methods for making various oxygen-scavenging polymers useful in the present invention;

Fig. 2 is a vertical cross-section of a multilayer preform useful in making a beverage container according to one embodiment of the present invention;

- 30 Fig. 3 is a side elevational view of a multilayer pressurized container made from the preform of Fig. 2;

Fig. 4 is a horizontal cross-section taken along line 4-4 of Fig. 3, showing the multilayer sidewall of the container;

- Fig. 5 is a vertical cross-section of a blow-molding apparatus for making the
- 35 container of Fig. 3;

Fig. 6 is a vertical cross-section taken along line 6-6 of Fig. 3, showing one foot of the container base;

Fig. 7A is an enlarged fragmentary cross-section of a crystallized neck finish and cap, according to one embodiment;

5 Fig. 7B is an enlarged fragmentary cross-section of an amorphous neck finish and cap, according to another embodiment;

Figs. 8A and 8B are side elevational views of a multilayer preform and resulting container according to another embodiment of the present invention;

10 Fig. 9 is a schematic sectional view through a preform for making a can according to an alternative embodiment;

Fig. 10 is a schematic sectional view of an intermediate article made from the preform of Fig. 9, including as a lower portion a can which is biaxially oriented up through the finish, and an upper portion which is removed and discarded;

15 Fig. 11 is a schematic sectional view through a preform according to another embodiment having a neck finish insert and multilayer body- and base-forming portions; and

Fig. 12 is a graph illustrating changes in internal temperature and pressure over a typical pasteurization cycle, for a prior art 12-oz glass container filled with a juice product carbonated at 2.5 volumes; and

20 Figs. 13A-13K are a series of steps showing oxygen consumption by the aliphatic chain of the alpha-hydrogen carbonyl group.

#### Detailed Description

The present invention relates to aromatic ester scavenging polymers, having alpha-hydrogen carbonyl oxygen-scavenging groups, which can be blended or copolymerized (includes transesterification) with an aromatic polyester polymer, or used in a layer structure with the polyester polymer, to form a transparent article for the storage of oxygen-sensitive products. In a principal embodiment, described herein, the scavenging polymer is used for injection molding substantially transparent preforms, and blow molding of those preforms to form substantially transparent containers for beer, juice, ketchup and other oxygen-sensitive products.

30 The particular materials, wall thicknesses, layer structures and container design will depend upon the particular product application and conditions of filling, sterilization and use, but the common goal is to provide active barrier protection in a cost-effective manner for use with commercially-

available aromatic polyester resins (e.g., PET and PEN), such that the final container provides substantial transparency, is lightweighted and has the structural integrity required of a commercially-acceptable polyester container.

In the present embodiment, the aromatic ester oxygen-scavenging polymer should  
5 have chemical and physical properties that allow substantially transparent preforms and packaging structures to be formed partially or entirely therefrom. For example, apart from their oxygen-scavenging potential during use, the scavenging polymer should be substantially chemically inert under the conditions used to make preforms and packaging structures, and under the unfilled storage conditions of such preforms and packaging structures. For example, it may  
10 be desirable that the end groups of the polymer have reduced chemical reactivity. Preferably, the oxygen-scavenging polymer should not substantially deleteriously affect the transparency, melting temperature, viscosity or other processing parameters of the polymer composition. Moreover, in select embodiments the oxygen-scavenging polymer should be substantially chemically inert towards foods and/or beverages intended to be stored within the packaging  
15 structure.

By way of introduction, some well-known principals of PET manufacture will first be described. A diacid may be condensed with a glycol, or a hydroxy acid self-condensed, in order to form a linear polyester such as PET. Fig. 1A (taken from K. Wissermal and H.J. Arpe, Industrial Organic Chemistry, Section 14.4, Applications of Terephthalic Acid and  
20 Dimethyl Terephthalate, Verlag Chemical Press, pages 349-351 (1978)), describes a two-step process for PET manufacture. In a first step, dimethyl terephthalate (DMT) is trans-esterified with ethylene glycol with a loss of  $\text{CH}_3\text{OH}$ ; as an alternative first step (not shown), terephthalic acid (TPA) may be esterified with ethylene glycol producing a loss of  $\text{H}_2\text{O}$ . This first step is carried out at a temperature on the order of 100-150°C and a pressure of 10-70 bar, in the  
25 presence of for example copper, cobalt or zinc acetate catalysts. The resulting intermediate product is bis(2-hydroxyethyl) terephthalate. As a second step, the intermediate product undergoes catalytic polycondensation to produce PET; this is typically done at a temperature of approximately 10-20°C above the melting point of PET (246°C), under vacuum, and usually with a catalyst, such as  $\text{Sb}_2\text{O}_3$ . During the polycondensation step, ethylene glycol is removed.  
30 The resulting PET melt is then cooled and granulated. In Fig. 1A and subsequent figures, the atoms/groups being removed are shown in a box with an arrow, for ease of identifying the reaction sites.

PET is a thermoplastic polyester, used in strain-oriented form as both a packaging film and as blow-molded soft-drink containers. It is commercially available as either a homopolymer or more typically as a copolymer with small amounts of other monomers to enhance processability or performance (e.g., thermal resistance). For example, there are well-known PET copolymers which include varying amounts, normally up to about 10 mole percent of other monomers, which are compatible with the PET and do not substantially detract from the desired PET structural properties or processing parameters. These may also be used in the context of the present invention. Thus, as used herein "PET" is meant to include PET homopolymer and copolymers.

10

#### Fig. 1B: REVPET

Fig. 1B illustrates a method of making an oxygen-scavenging polymer referred to herein as "REVPET". The repeating unit for REVPET (shown in Fig. 1B) has the same numbers of carbon, oxygen and hydrogen atoms, and thus the same molecular weight, as the repeating unit for PET (shown in Fig. 1A). As a result, REVPET has a high level of compatibility with PET which enables it to be blended and/or copolymerized with PET, or used in a layer structure with PET, wherein the PET can be biaxially oriented and remain substantially transparent. As used herein, "transparent" is meant to include substantially transparent in that it is commercially acceptable to have some reduction in light transmission caused by crystallization or the like in what is generally referred to as a transparent container. A definition of transparency is set forth hereinafter with regard to ASTM Method D1003.

The structural difference between REVPET and PET (as illustrated in Figs. 1A-1B), is that in REVPET the backbone oxygen in each ester (COO) group is adjacent to the aromatic ring, and thus the CH<sub>2</sub> group (adjacent to the C of the ester group) provides an alpha-hydrogen carbonyl functional group for oxygen scavenging.

REVPET has two alpha-hydrogen carbonyl groups per repeating unit, which provides a relatively high degree of oxygen scavenging. The two ester groups, single aromatic ring and two methyl groups in the backbone provide a match of solubility parameters with PET, permitting use in blends, copolymers, and layer structures with good adhesion between layers and transparency.

The Table in Appendix C, just before the claims at page 49, lists various properties of REVPET (and other polymers shown in Figs. 1B-1K) for comparison with PET.

The properties include:

	$T_G$	glass transition temperature
	$T_m$	melting temperature
5	SOL	solubility parameter (Van Krevelen, discussed hereinafter)
	ADEN	density of amorphous polymer
	CDEN	density of crystallized polymer
	PERM	nitrogen permeability of amorphous polymer
10	AROM	molecular weight percentage of aromatic rings to total weight of scavenging polymer (per repeating unit); exception for bisphenol A where weight percentage of aromatic rings includes $\text{CH}_3\text{-C-CH}_3$ between the 2 rings
	CARB	molecular weight percentage of C and O in carbonyl group to total weight of scavenging polymer (per repeating unit); exception for nylons where number multiplied by 1.5 to include impact carbonyl has on adjacent NH.
15	ALPHA	molecular weight percentage of $(\text{CH}_2)_n$ in aliphatic group adjacent carbonyl carbon to total weight of scavenging polymer (per repeating unit); exception for nylons where number multiplied by 1.5 to include impact carbonyl has on adjacent NH.

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The first column,  $T_G$ , is an important parameter as previously discussed. The scavenging polymer should have a  $T_G$  at least  $10^\circ\text{C}$  below the orientation temperature of the polyester polymer with which it is combined (in the transparent article). REVPET has a  $T_G$  of  $43^\circ\text{C}$ , well below the typical orientation temperature of PET (e.g.,  $90^\circ\text{C}$  and above). The second column,  $T_m$ , shows that REVPET has a melting temperature of  $214^\circ\text{C}$ . The third column, the solubility parameter, shows that REVPET has the exact same solubility parameter (20.53) as PET. The fourth and fifth columns, the densities of the amorphous and crystalline polymers, are identical for REVPET and PET. Also, the solubility to nitrogen (PERM) is identical.

The last three columns, AROM, CARB, and ALPHA, attempt to quantify the molecular weight percent of 3 functional groups in the scavenging polymer which have a significant effect on performance. AROM, the weight percentage of the aromatic rings, has a large effect on  $T_G$ , i.e., increasing the percentage of aromaticity, generally, increases the  $T_G$ . For

30

example, REVPET has a rather low  $T_G$  compared to later described scavenging polymers. A higher  $T_G$  would provide a higher use temperature, and reduce the potential that the scavenging polymer will crystalline (or opacify) during the orientation process. CARB, the weight percentage of the carbonyl (CO), has a large effect on the rate of scavenging, i.e., the more alpha-hydrogen carbonyl groups, the greater the rate of scavenging. ALPHA, the weight percentage of aliphatic chain, has a large effect on the long-term scavenging potential, i.e., an increase in chain length increases the potential sites for scavenging and thus increases the shelf life which the package can provide. Example calculations for these parameters are set forth in Appendix C.

Preferred ranges are:

10                    AROM:        30 to 70  
                     CARB:        5 to 30  
                     ALPHA:      5 to 30

The reaction illustrated in Fig. 1B may be implemented in accordance with various well-known processes as follows:

15                    PREPARATION OF POLY HYDROQUINONE SUCCINATE, REVPET, BY  
                     THE INTERFACIAL POLYCONDENSATION PROCESS (see W.M. Eareckson III,  
                     J. Polymer Science, 40, 399 (1959)):

20                    To a blender is added 0.05 mole of hydroquinone, and 0.1 mole of sodium  
                     hydroxide in 300ml (millilitres) of water. A solution of 3.0 g (grams) of sodium lauryl  
                     sulfate in 30ml of water is also added. The speed is regulated so that at low speed a  
                     second solution of 0.05 moles of succinoyl chloride in 150ml of hexane is quickly added.

This mixture is stirred at high speed for 10 minutes then poured into acetone. The polymer is filtered, washed with water, and dried to provide an 80%+ yield.

25                    Bisphenol A can be substituted for hydroquinone to make a higher  $T_G$  polymer  
                     (see Fig. 1J below).

Other acid chlorides can be substituted for succinic acid chloride to increase the scavenging potential or adjust  $T_G$ . A substitution of glutaric acid for succinic acid would give modified REVPET, described below. When using an aliphatic acid, it may be advantageous that pyridine be substituted for sodium hydroxide and water in the above reaction.

30                    ANOTHER METHOD OF PREPARATION OF HYDROQUINONE  
                     SUCCINATE (REVPET)(see British Patent 636,429 to Eric R. Wallsgrove and Frank Reeder,  
                     issued April 26, 1950):

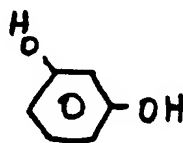


10 parts hydroquinone diacetate is combined with 9.5 parts succinic acid and .1 parts p-Me-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H. They are heated at 180°C for 45 minutes, then 200-220°C for 1 hour, then 280°C for 3 hours all at atmospheric pressure, and finally 280°C for 3 hours at 1 mm Hg while nitrogen is bubbled through the molten mix.

5

As a further alternative, one can use isomers of the aforementioned monomers to make small adjustments in T<sub>G</sub> and larger adjustments in crystallinity levels. For example, one can substitute resorcinol:

10



at various molar concentrations for hydroquinone in the above methods for making REVPET; e.g., substituting 20 molar percent resorcinol would raise the T<sub>G</sub> by 2°C and reduce the crystalline nature by 50%.

#### Fig. 1C: Modified REVPET

Fig. 1C illustrates a method of making a second oxygen-scavenging polymer referred to herein as modified REVPET. The only difference between modified REVPET and REVPET is in the addition of one CH<sub>2</sub> in the aliphatic chain. As shown in the Table of Appendix C at page 49, modified REVPET has a solubility parameter (SOL) of 20.18, compared to 20.53 for PET. The extra carbon atom (in the aliphatic carbon chain) also reduces the T<sub>G</sub>, compared to the T<sub>G</sub> of REVPET. It may be desirable to add additional functional groups which would increase the T<sub>G</sub>. Examples of such modifications to the T<sub>G</sub> are described below for the methods/polymers of Figs. 1D-1K.

The process conditions for making modified REVPET are similar to those for making REVPET described above, wherein glutaric acid is substituted for succinic acid.

#### Fig. 1D: Polymer 1D

Fig. 1D shows a method of making another aromatic ester oxygen-scavenging polymer useful in the present invention, and referred to herein as polymer-1D. The repeating unit (shown in Fig. 1D) includes two alpha-hydrogen carbonyl groups, two ester groups, six

aromatic rings (two in the backbone and four on side chains), and one 3-carbon aliphatic group. The six aromatic rings increase the  $T_G$  (compared to PET), however the extra carbon atom in the aliphatic chain ( $3CH_2$ ) decreases the  $T_G$  (compared to the 2-carbon chain in PET). Thus by changing the various functional groups in the polymer, and/or similarly by varying the relevant proportions of the functional groups in the polymer, one can generally increase or decrease the  $T_G$ . These functional groups, and their regularity, may similarly affect the crystallization rate. Generally, a skilled person will now be able to determine the appropriate proportions of various groups for a given application, based upon the process conditions necessary to achieve a transparent oxygen-scavenging polymer including biaxially-oriented PET, and whether the aromatic ester polymer is blended or copolymerized with the PET, or alternatively is provided in a separate layer structure. Similarly, the starting materials may be varied depending upon what is commercially available and the costs of such components.

#### METHOD OF PREPARING POLYMER-ID FROM DIMETHYL ESTER OF DIPHENIC ACID, DISTYRENE GLYCOL AND DIMETHYL ESTER OF GLUTARIC ACID

In a sealed 3-neck 1-liter flask, with agitation, mix 0.25 mole of the two dimethyl esters and 1.1 moles of the glycol, and 0.0464g of cobalt acetate. Pressurize vessel to 10 psi and raise heat slowly with agitation to a slight boil about  $180^\circ\text{C}$ . Slowly raise temperature just to maintain slight boil while maintaining 10 psi until  $250^\circ\text{C}$ . Hold at  $250^\circ\text{C}$  for 2 hours. Then release pressure and switch to vacuum. Add 0.033g  $SbO_3$ , mixed in a small amount of dimethyl ester of glutaric acid. Raise temperature to  $280^\circ\text{C}$ . Hold pressure at 1 torr for 4 hours.

#### Fig. 1E: Polymer-1E

Fig. 1E shows another aromatic ester oxygen-scavenging polymer for use in the present invention. The repeating unit (shown in Fig. 1E) includes two alpha-hydrogen carbonyl groups, two esters, a 4-carbon atom aliphatic chain, and one aromatic structure (including two rings) in the backbone. While the 4-carbon aliphatic chain would reduce the  $T_G$  (compared to the 2-carbon chain in PET), the extra aromatic ring (compared to a single ring in PET) would increase the  $T_G$ . Polymer-1E has an estimated  $T_G$  of  $71^\circ\text{C}$  (see Appendix C on page 49) which is just above that of PET ( $70^\circ\text{C}$ ) and in the preferred range. Polymer-1E is commercially available from Dow Chemical, Midland, Michigan USA.

The relative proportions of components may be adjusted for a specific application. Generally, to increase the level of oxygen-scavenging, one would increase the level of alpha-hydrogen carbonyl groups by substituting more adipic acid and reducing the amount of

diglycidyl ether of bis-phenol A. A modified version of polymer-1E made with succinic acid has a  $T_g$  of 70°C.

#### Fig. 1F: Polymer-1F

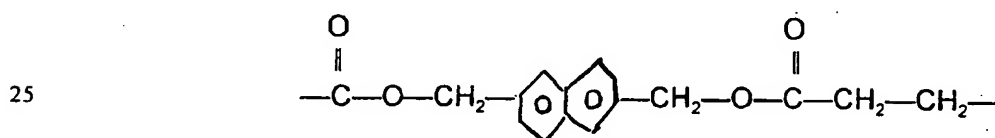
Fig. 1F shows a further alternative aromatic ester oxygen-scavenging polymer referred to herein as polymer-1F. The repeating unit includes two alpha-hydrogen carbonyl groups, two ester groups, a 4-carbon aliphatic chain in the backbone, and one aromatic side chain. Again, the relative proportions of ingredients can be modified for a specific application.

An alternative polymer made with succinic acid -- instead of adipic -- would have a higher  $T_g$  (see Table in Appendix C on page 49). Further increases in  $T_g$  are possible by using distyrene oxide (instead of styrene oxide) with adipic acid, or distyrene glycol (instead of styrene oxide) with succinic acid.

#### Fig. 1G: REVPEN

Fig. 1G illustrates the process of making a further scavenging polymer, referred to herein as REVPEN. This is similar to REVPET (Fig. 1B), but is based upon naphthalene rather than benzene. REVPEN is prepared by condensing 1,2 or 2,6 naphthalene diacetate and dimethyl ester of succinic acid. The reaction conditions are similar to those for making REVPET, but at a higher temperature (e.g., 300°C) in the final stage.

A modified version of REVPEN is shown below, having an additional  $\text{CH}_2$  group at each side of the aromatic ring:



#### Fig. 1H: POLYMER-1H

Fig. 1H shows a random polymer of groups A, B, and C, where A is provided by naphthalene dicarboxylate (NDC), B is provided by adipic acid, and C is provided by ethylene glycol (where the atoms/molecules lost are shown in a box with an arrow). The resulting polymer-1H is basically a random copolymer of PEN and aliphatic acid. For every two naphthalene components, there is one aliphatic component (molar parts). This is a solid, highly crystalline polymer, which is stable at higher temperatures. This enables the polymer to be easily

dried and solid stated to build up the molecular weight. Polycondensation polyesters, having highly crystalline structures and high melt temperatures, can be solid stated to increase the molecular weight.

Transparent multilayer blow-molded bottles have been made from preforms, including layers of virgin PET and layers of polymer-1H. There is good adhesion between the layers, which prevents delamination.

More generally, the aliphatic acid component (here adipic acid) can have a  $(CH_2)_n$  group where  $n = 2$  to 10.

#### METHOD OF PREPARING A COPOLYMER OF DIMETHYL 2,6 10 NAPHTHALENEDICARBOXYLATE/ADIPIC ACID WITH ETHYLENE GLYCOL-- POLYMER-1H

In a 3-liter 2-neck reaction flask, with agitation, mix 2.4 moles (580g) NDC, 1.2 moles (175g) adipic acid, 8 moles (496g) ethylene glycol and 0.4725g  $SbO_3$ . Purging nitrogen through the system at 8 psi, heat sample to 175°C and hold for 10 minutes. Then raise temperature to 210°C and hold for 5 minutes. Again raise the temperature to 240°C and hold for 1 hour after sample becomes clear. Raise temperature to 260°C and hold for 1 hour. Raise temperature to 275°C and hold for 3 hours. Switch from pressure to vacuum and hold at 275°C under steady vacuum for 4 more hours. Final vacuum should be below 1 torr.

20

#### Fig. 11: Polymer-11

In Fig. 11, there is shown a substituted hydroxy acid monomer with an acetate on one end and an ethyl, methyl ester on the other end; this monomer reacts with itself to produce another oxygen-scavenging polymer having the repeating unit shown. Polymer 11 has one aromatic ring, one ester group, one alpha hydrogen carbonyl group, and a 2-carbon aliphatic chain.

25

#### METHOD OF POLYMERIZING 4-(ACETYLOXY)BENZENE PROPANOIC ACID TO MAKE POLYMER-11

In a sealed 2-neck 1-liter flask, with agitation, place 1 mole (136g) of the acid, 0.13g of  $SbO_3$  and 0.19g cobalt acetate. Heat to 150°C with slight agitation under a nitrogen purge of 0.25 l/minute at 10 psi. Raise heat until a slight boil occurs, then reduce purge but maintain 10 psi. Continue to raise temperature to maintain boil and 10 psi to a temperature of 180°C. Hold pressure and temperature for 40 minutes. Pull vacuum and raise temperature to 210-220°C for 90 minutes.

35

Fig. 1J: Polymer-1J

Fig. 1J shows condensation of bisphenol-A diacetate and adipic acid to make the polymer-1J, having two alpha-hydrogen carbonyl groups, two esters, one aromatic backbone structure (with two rings), and a 4-carbon chain aliphatic group. As shown in the Table in Appendix C at page 49, polymer-1J has relatively high  $T_G$  of 91 °C. A modified polymer listed just below polymer-1J in the Table, identified as "Bis A Acetate/Suberic Acid", has a lower  $T_G$  of 79 °C, which is in the preferred range for use with PET orientation temperatures.

The following process may be used to prepare a polymer from bisphenol A diacetate and suberic acid:

10 PREPARATION OF A POLYMER FROM BISPENOL A AND SUBERIC ACID (see for example Preparative Methods Of Polymer Chemistry, 2nd Edition, Sorensen, Campbell, page 149):

In a first step, diacetate of bisphenol A is prepared by dissolving 11g (grams) of bisphenol A in a solution of 9g (.22 mole) sodium hydroxide in 45ml water in a 250ml Erlenmeyer flask. The mixture is cooled in an ice bath and a small quantity of ice is added to the flask. Then, 22.4g (.22 mole) acetic anhydride is added and the flask is shaken vigorously in an ice bath for 10 minutes. The white solid is filtered, washed with water, and recrystallized from ethanol.

A mixture of bisphenol A diacetate 312g (1 mole), suberic acid 174g (1 mole), 0.60g toluenesulfonic acid (monohydrate) is placed in a 2-liter, 2-neck flask with agitator. The flask is purged with nitrogen while agitating for 20 minutes. The temperature is then raised to 180 °C while agitating and purging with nitrogen at ambient pressure. Acetic acid distills as the temperature is slowly raised from 180 °C to 250 °C while the pressure is slowly reduced to about 1 torr. The melt is maintained at 250 °C and 1 torr for 1 hour.

When using an aliphatic acid, it may be advantageous that pyridine be substituted for sodium hydroxide and water in the above reaction.

Fig. 1K: Polymer-1K

30 Fig. 1K shows a ring opening polymerization of a cyclic ester. Caprolactone (cyclic) is combined with a cyclic carbonate ester, to produce polymer-1K. The resulting polymer has two alpha-hydrogen carbonyl groups, a two-ring aromatic structure in the backbone (bisphenol A) and a five-carbon aliphatic chain. As shown in the Table in Appendix C at page

49, polymer-1K has a  $T_g$  of 85°C, in the preferred range for use with PET polymers. Polymer-1K has a good match of solubility parameter with PET (20 vs. 20.53).

Methods for polymerizing cyclic carbonate esters and lactones are described in George Odian, Principles of Polymerization, 3d edition, John Wiley & Sons, Inc., New York  
5 (1991), pp. 569-573.

The above-described oxygen-scavenging polymers (shown in Figs. 1B-1K) may be used alone, or blended or copolymerized with an aromatic polyester polymer, preferably a PET or PEN polymer, to provide an oxygen-scavenging material. This material may then be incorporated in a packaged container structure to provide a desired level of oxygen scavenging  
10 property, as described below.

#### Pasteurizable Beer Container

Figs. 2-6 illustrate a method of making a transparent one-liter pasteurizable beer container utilizing a multilayer structure and oxygen-scavenging polymer of this invention.

15 An injection-molded multilayer preform 30 is shown in Fig. 2. The preform is substantially cylindrical, as defined by vertical centerline 32, and includes an upper neck portion or finish 34 integral with a lower body-forming portion 36. The neck portion has a top sealing surface 31 which defines the open top end of the preform, and a generally cylindrical exterior surface with threads 33 and a lowermost flange 35. Below the flange is the body-forming  
20 portion 36 which includes an upper cylindrical portion 41, a flared shoulder-forming portion 37 which increases radially inwardly in wall thickness from top to bottom, a cylindrical panel-forming section 38 having a substantially uniform wall thickness, and a thickened base-forming section 39 which is thicker than the panel-forming section 38. The closed bottom end of the preform 40 is substantially hemispherical and may be thinner than the base-forming portion 39.

25 Preform 30 has a three-material, five-layer (3M, 5L) structure and is substantially amorphous and transparent. The multiple preform layers comprise, in serial order: outer layer 42 of virgin PET, outer intermediate layer 43 of EVOH, central core layer 44 of oxygen-scavenging material, inner intermediate layer 45 of EVOH, and inner layer 46 of virgin PET. The virgin PET may be any commercially available, bottle-grade PET homopolymer or copolymer having  
30 an intrinsic viscosity of about 0.90 dl/g. The EVOH is commercially available with a 32 mole % ethylene content from Evalca, Omaha, Nebraska, USA, or Kuraray Co. Ltd., Osaka, Japan. The core layer is REVPET as previously described (Fig. 1B), having an intrinsic viscosity of about

0.70 dl/g, a  $T_G$  of 43°C, and a melting point of 214°C. The REVPET polymer includes 150 micrograms of cobalt per gram of REVPET polymer, added as cobalt neodeconoate.

The preform 30 is adapted for making the 1.0 liter pasteurizable pressurized container for beer, shown in Fig. 3. The preform 30 has a height of about 150mm, and an outer diameter in the panel-forming section 38 of about 23.8mm. The total wall thickness of the panel-forming section 38 is about 4.1mm; the thickness of the various sidewall layers are: outer and inner layers each about 1.1mm thick; inner and outer intermediate layers each about 0.1mm thick; and core layer about 1.7mm thick. For pasteurizable carbonated beverage containers of about 0.3 to 1.5 liters in volume, having a panel wall thickness of about 0.25 to about 0.38mm, and filled at about 2.0 to 4.0 volumes of CO<sub>2</sub> aqueous solution, the preform panel-forming section 38 preferably undergoes an average planar stretch ratio of about 13.0 to 14.5. The planar stretch ratio is the ratio of the average thickness of the preform panel-forming portion 38 to the average thickness of the container panel 86 (as shown in Fig. 3); the average is taken along the length of the respective preform and container portions. The average panel hoop-stretch is preferably about 4.0 to 4.5, and the average panel axial stretch is about 3.0 to 3.2. This produces a container panel 86 with the desired biaxial orientation and visual transparency. The specific panel thickness and stretch ratio selected depend on the dimensions of the bottle, the internal pressure, and the processing characteristics (as determined for example by the intrinsic viscosity of the particular materials employed).

The preform shown in Fig. 2 may be injection molded by a sequential metered process described in U.S. Patent Nos. 4,550,043; 4,609,516; 4,710,118; 4,781,954; 4,990,301; 5,049,345; 5,098,274; and 5,582,788, owned by Continental PET Technologies, Inc. of Bedford, New Hampshire. In this process, predetermined amounts of the various materials are introduced into the gate of the preform mold as follows: a first shot of virgin PET which forms partially-solidified inner and outer preform layers as it moves up the cool outer mold and core walls; a second shot of EVOH which will form the inner and outer intermediate layers; and a third shot of the oxygen-scavenging material which pushes the EVOH up the sidewall (to form thin barrier layers) and forms a central core layer of oxygen-scavenging material. A final shot of virgin PET may be used to clear the nozzle and finish the bottom of the preform with virgin PET.

After the mold is filled, the pressure is increased to pack the mold against shrinkage of the preform. After packing, the mold pressure is partially reduced and held while the preform cools. In a standard process, each of the polymer melts are injected into the mold at

a rate of about 10-12 grams per second, a packing pressure of about 7500 psi ( $50 \times 10^6 \text{ N}\cdot\text{m}^{-2}$ ) is applied for about 4 seconds, and the pressure is then dropped to about 4500 psi ( $30 \times 10^6 \text{ N}\cdot\text{m}^{-2}$ ) for the next 15 seconds, after which the pressure is released and the preform is ejected from the mold. Increasing the pressure above these levels may force higher levels of interlayer bonding, which may include chain entanglement, hydrogen bonding, low-level interlayer crystallization and layer penetration; these may be useful in particular applications to increase the resistance to layer separation in both the preform and container. In addition, increased pressure holds the preform against the cold mold walls to solidify the preform without haze, i.e., loss of transparency, at the minimum possible cycle time. Still further, faster injection rates may yield higher melt temperatures within the injection cavity, resulting in increased polymer mobility which improves migration and entanglement during the enhanced pressure portion of the injection cycle, and thus increases the delamination resistance. As an additional option, increasing the average preform temperature and/or decreasing the temperature gradient through the preform wall may further reduce layer separation by minimizing shear at the layer boundaries during preform expansion.

Fig. 5 illustrates a stretch blow-molding apparatus 70 for making the container 80 from the preform 30. More specifically, the substantially amorphous and transparent preform body-forming section 36 is reheated to a temperature above the glass transition temperatures of the inner/outer PET and core oxygen-scavenging layers, and the heated preform then positioned in a blow mold 71. A stretch rod 72 axially elongates (stretches) the preform within the blow mold to insure complete axial elongation and centering of the preform. The thickened base-forming region 39 of the preform resists axial deformation compared to the panel- and shoulder-forming portions 38 and 37. This produces greater axial elongation in the resulting panel and shoulder portions of the container. A blowing gas (shown by arrow 73) is introduced to radially inflate the preform to match the configuration of an inner molding surface 74 of the blow mold. The formed container remains substantially transparent but has undergone strain-induced biaxial orientation to provide the increased strength necessary to withstand carbonation and the increased temperature and pressure of pasteurization.

Fig. 3 shows the 1.0 liter pasteurizable multilayer beverage bottle 80 made from the preform of Fig. 2. The preform body-forming portion 36 has been expanded to form a transparent biaxially-oriented container body 81. The upper thread finish 34 has not been expanded, but is of sufficient thickness or material construction to provide the required strength.



The bottle has an open top end 82 and receives a screw-on cap (see Figs. 7A-7B). The expanded container body 81 includes:

- 5 (a) an upper flared shoulder section 83 with an outwardly-protruding profile, and which generally increases in diameter from below the neck finish flange 35 to a cylindrical panel section 86; it is preferable to provide a rounded (hemispherical) shoulder 83 because this shape maximizes the biaxial orientation and minimizes the applied stress levels. Higher orientation and lower stress will lower the container volume increase due to creep at elevated temperatures (during pasteurization), and thus minimize any drop in fill level; also, it is preferable to  
10 provide a small transition radius 84 between the neck finish 34 and shoulder 83 to minimize the unoriented area at the top of the shoulder (an unoriented area may be prone to creep);
- 15 (b) the substantially cylindrical panel section 86 preferably has a relatively tall and slender configuration, i.e., a height to diameter ratio on the order of 2.0 to 3.0, in order to minimize the stress in the sidewall (and minimize creep); relatively shallow transition regions 87 and 88 are provided at the upper and lower ends of the panel 86, respectively; larger transition areas would be more likely to expand (straighten) during pasteurization and cause a volume increase (fill level drop); for the same reason, preferably no ribs (which may creep) are provided in the panel  
20 section 86;
- 25 (c) a footed base 90 has a substantially hemispherical bottom wall 92 and for example, five legs 91 which extend downwardly from the bottom wall to form five foot pads 93 on which the container rests; the legs 91 are symmetrically disposed around the container circumference; in addition, it is preferable to provide a high depth base, i.e., close to a hemispherical base, in order to maximize strength and resistance against creep; it is also preferable to provide an angled foot pad which can move outwardly under creep and yet remain within the diameter of the container.

The panel-forming section 38 of the preform may be stretched at an average  
30 planar stretch ratio on the order of 13.0 to 14.5; the virgin PET layers of the resulting panel section 86 have an average strain-induced crystallinity on the order of 20% to 30%, and preferably on the order of 25% to 29%. The shoulder 83 undergoes an average planar stretch

ratio of about 10.0 to 12.0; the virgin PET layers of the resulting shoulder 83 have an average crystallinity of about 20% to 25%. The hemispherical bottom wall 92 in the base undergoes an average planar stretch of about 5.0 to 7.0, and the virgin PET layers have about 5% to 15% average crystallinity; the legs and feet undergo an average planar stretch of about 13.0 to 14.0, and the virgin PET layers have about 20% to 26% average crystallinity. The core oxygen-scavenging layer has an average level of crystallinity of about 2% less than the virgin PET layers in each respective area of the container, e.g., 18-28% in the panel, 18-23% in the shoulder, 3-12% in the hemispherical bottom wall, and 18-24% in the legs and feet.

Fig. 4 shows a cross-section of the panel wall 86, including inner layer 95 of virgin PET, core layer 96 of oxygen-scavenging material, outer layer 97 of virgin PET, and inner and outer intermediate layers 98, 99 of EVOH. In this embodiment, the relative percent by total weight of the various layers in the panel section are about 30% for inner layer 95, about 40% for core layer 96, and about 30% for outer layer 97 (the EVOH layers 98, 99 together are less than 2 weight percent). The EVOH inner intermediate layer 98 will become permeable to oxygen when water vapor from the product permeates through the inner PET layer 95; this will enable oxygen in the container to permeate layers 95 and 98 and reach core layer 96 where it is consumed. In contrast, outer intermediate layer 99 remains relatively dry and resists exterior oxygen from entering the container. In an alternative embodiment, it may be desirable to substitute for REVPET in the core layer a blend of PET and REVPET, where 5-20 weight percent of the core layer is REVPET; this would provide a higher  $T_g$ .

The preferred features of the footed container base are shown more clearly in Fig. 6. As a basis of comparison, a known five-foot PET disposable carbonated beverage container (non-pasteurizable) has a relatively low base profile ( $\theta$  of about  $45^\circ$ ). In contrast, the present base preferably has a relatively high base profile on the order of  $60^\circ$  or better. Fig. 6 shows in solid lines a base having a full hemisphere A where  $\theta = 90^\circ$ , and in dashed lines a truncated hemisphere B where  $\theta = 60^\circ$ ,  $\theta$  being the angle that the radius R, defining the hemispherical bottom wall 92, extends from the vertical centerline (CL) of the container body. The relative heights of the base are illustrated as  $H_A$  for the full hemi, and  $H_B$  for the truncated hemi. It is preferable to provide a base height between  $H_B$  and  $H_A$ , and more preferably where  $\theta$  is greater than  $65^\circ$ .

In addition, it is preferable to provide an angled foot pad. The foot pad extends between points G and K on the leg 91 (for  $\theta = 90^\circ$ ), or 91' (for  $\theta = 60^\circ$ ). The foot pad is

preferably spaced a distance  $L_F$  from the vertical centerline CL to a point G which is vertically aligned with a center point of radius  $R_G$ . Radius  $R_G$  forms the outer edge of the foot pad. The foot pad forms an acute angle  $\alpha$  with a horizontal surface 102 on which the base rests.

Preferably,  $L_F$  is on the order of  $0.32R$  to  $0.38R$ , and  $\alpha$  is on the order of  $5^\circ$  to  $10^\circ$ , to allow each  
5 foot pad and leg to move out under creep, and yet remain within the diameter of the container.

Fig. 7A is an enlarged cross-section of an opacified neck finish enclosure according to one embodiment. More specifically, the unoriented neck finish 110 has been thermally crystallized (opacified) by for example, high-temperature exposure; this increases the strength and enhances its resistance to the increased temperature and pressure of pasteurization.  
10 The heat-treated area may extend just below the flange 111. A cap 116 has an annular ring 117 of a resilient material (e.g., plastisol or other thermoplastic elastomer) which seals the top sealing surface 112 of the neck finish. If there is any deformation of the neck finish during pasteurization, the liner 117 deforms to ensure a tight seal and prevent leakage.

In an alternative embodiment shown in Fig. 7B, a substantially amorphous and  
15 unoriented neck finish 120 is provided, i.e., it has not been crystallized. In this case, the amorphous neck finish is provided with a laminated foil liner 124, which lies within an inner surface of a cap 126, and which may, for example, be heat sealed or adhesively sealed to the top sealing surface 122 of the neck finish. Again, if there is any deformation of the neck finish, the liner 124 ensures a tight seal to prevent leakage.

20

#### Other Embodiments

Fig. 8 shows another embodiment comprising a 1/2-liter non-pasteurizable beer container. In this example, the bottler extensively filters the beer, so that the bottle need not be subjected to heat treatment. A preform 200 for making the bottle is shown in Fig. 8A, including  
25 thread finish 201, flared shoulder portion 202, cylindrical body portion 203, and closed bottom 204. The preform 200 and resulting blow-molded container 210 (Fig. 8B) have a five-layer structure (not shown), including inner and outer layers of virgin PET (62 weight percent by total weight), a core layer of post consumer PET (35 weight percent), and 2 thin intermediate layers of REVPET homopolymer, as the oxygen-scavenging polymer (3 weight percent). The REVPET  
30 has an intrinsic viscosity of 0.70 dl/g, a  $T_g$  of  $43^\circ\text{C}$  and a melting point of  $214^\circ\text{C}$ . The virgin PET is Shell 8006, having a 0.80 IV nominal, and including 4 molar percentage isothalic acid copolymer (available from Shell Oil Company, Houston, Texas, U.S.A.). In contrast to the

previous embodiment, this beer bottle has a champagne base 212, including a standing ring 214 which surrounds a central push-up dome 216. This container provides a shelf life for beer of about 16 weeks.

Another embodiment comprises a relatively wide-mouth container, such as a can, including the oxygen-scavenging material of the present invention. The can may be formed from a preform according to the process described in U.S. Patent No. 4,496,064 to Beck et al., which issued January 29, 1985, and is hereby incorporated by reference in its entirety. Fig. 9 shows a preform 142 (from the Beck patent) which includes a support flange 144, a thin upper body portion 145 which flares into a thick generally cylindrical main body portion 146, and a generally hemispherical bottom portion 148. The Beck process enables a high degree of biaxial orientation to be obtained in all portions of the resulting container, so that the container has economical thin walls and the desired strength characteristics. In this case, the preform is expanded to form an intermediate article 150, which includes a lower portion 152 in the form of the desired container, and an upper portion 154. The lower portion includes a cylindrical body 132, concave bottom 134, tapered shoulder 136, mouth 138, and annular flange 130. The upper portion is severed from the flange 130 at point 164 (as by cutting or laser trimming), and may be discarded, or ground and the material reused. It is generally not necessary to thermally crystallize or otherwise reinforce the upper end of the container, because the biaxial orientation provides the necessary strength. A method of trimming the expanded preform to remove the upper unoriented portion is described in U.S. Patent No. 4,539,463 to Piccioli et al., which issued September 3, 1985, and is hereby incorporated by reference in its entirety.

Yet another method for providing a multilayer expanded preform container with a crystallized neck finish is described in U.S. Serial No. 08/534,126, entitled "Preform And Container With Crystallized Neck Finish And Method Of Making The Same," which was filed September 26, 1995 by Collette et al. (docket no. 7191), and is hereby incorporated by reference in its entirety. As described therein, an indexer (e.g., rotary or oscillatory) has two faces, each with a set of preform molding cores, and simultaneously positions the two core sets in two different sets of preform molding cavities. In the first set of cavities (first molding station), a high  $T_G$  amorphous or crystallized neck portion is formed on one set of cores, while in the other set of cavities (second molding station) a plurality of amorphous body-forming portions are formed on the other set of cores. The cores are sequentially positioned in each of the first and second molding stations. By simultaneously molding in two sets of cavities, an efficient process

is provided. By molding the neck and body-forming portions separately in different cavities, different temperatures and/or pressures may be used to obtain different molding conditions and thus different properties in the two preform portions. For example, as shown in Fig. 11, in one embodiment a polyester preform (for making a hot-fillable container) has a crystallized neck portion 180 of CPET; CPET is a terephthalic polyester with nucleating agents which render the polymer rapidly crystallizable during injection molding. CPET is sold by Eastman Chemical Company, Kingsport, Tennessee, USA. The body-forming portion 181 is a two-material, three-layer (2M, 3L) structure, including inner and outer layers of virgin polyethylene terephthalate (PET), and a core layer of the oxygen-scavenging polymer of this invention. The base-forming portion 182 is similar to the body-forming portion, but may include a core layer 183 of virgin PET in at least the bottom part and possibly extending through to the exterior of the preform. Alternatively, the core layer 183 in the base may be of a higher  $T_G$  polymer to enhance the thermal stability of the resulting container base; this is particularly useful with champagne-type container bases. The higher  $T_G$  polymer may be injected via a third extruder. Numerous alternative high-glass transition ( $T_G$ ) polymers may be used in place of CPET, such as: acrylate polymers; polyethylene naphthalate (PEN) homopolymers, copolymers or blends; polycarbonates; polyarylates; etc. As for the body-forming portion, numerous alternative polymers and layer structures are possible, incorporating PEN, ethylene/vinyl alcohol (EVOH) or MXD-6 nylon barrier layers, etc. The container is useful in a variety of applications, including refillable, pasteurizable, and hot-fillable containers.

As a further alternative, instead or in addition to providing the oxygen-scavenging material as part of the wall of a package, the material could be provided as an insert which can be added to a container. For example, the insert may consist of an oxygen-scavenging material coated with a polymer which is impermeable to oxygen when dry, and permeable when wet. The moisture in the product then permeates the coating, allowing oxygen to permeate to the oxygen-scavenging core layer.

#### Alternative Materials And Measurement Of Properties

The PET polymer as used herein includes homopolymers, copolymers, and blends of PET with other known compatible polymers, including other polyesters such as polybutylene terephthalate (PBT), polypropylene terephthalate (PPT), polyethylene naphthalate (PEN), and a cyclohexane dimethanol substituted PET copolymer known as PETG (available from Eastman

Chemical Company, Kingsport, Tennessee USA). Preferably, at least 90 mole % will be terephthalic acid and at least 90 mole % an aliphatic glycol or glycols, especially ethylene glycol.

Post-consumer PET (PC-PET) is prepared from PET plastic containers and other recyclables that are returned by consumers for a recycling operation, and has now been approved  
5 by the FDA for use in certain food containers. PC-PET is known to have a certain level of I.V. (intrinsic viscosity), moisture content, and contaminants. For example, typical PC-PET (having a flake size of one-half inch maximum), has an I.V. average of about 0.66dl/g, a moisture content of less than 0.25%, and the following levels of contaminants:

- PVC: < 100 ppm
- 10 aluminum: < 50 ppm
- olefin polymers (HDPE, LDPE, PP): < 500 ppm
- paper and labels: < 250 ppm
- colored PET: < 2000 ppm
- other contaminants: < 500 ppm

15

PC-PET may be used alone or in one or more layers for reducing the cost or for other benefits.

Another useful aromatic polyester is polyethylene naphthalate (PEN). PEN provides a 3-5X improvement in oxygen and carbon dioxide barrier properties and enhanced thermal resistance, at some additional expense, compared to PET. Polyethylene naphthalate  
20 (PEN) is a polyester produced when dimethyl 2,6-naphthalene decarboxylate (NDC) is reacted with ethylene glycol. The PEN polymer comprises repeating units of ethylene 2,6 naphthalate. PEN resin is available having an inherent viscosity of 0.67dl/g and a molecular weight of about 20,000 from Amoco Chemical Company, Chicago, Illinois. PEN has a glass transition temperature  $T_G$  of about 120°C, and a melting temperature  $T_m$  of about 267°C. PET and PEN  
25 may be blended or copolymerized in various amounts. In the ranges of about 0-20% PEN and 80-100% PEN, the material is crystalline, while from about 20-80% PEN the material is substantially amorphous.

Other useful biaxially-orientable aromatic polyesters include: polypropylene terephthalate, polybutylene terephthalate, polyethylene isophthalate, polycyclohexanedimethanol  
30 terephthalate, polypropylene naphthalate, polybutylene naphthalate, polycyclohexanedimethanol naphthalate.

The multilayer preform/container may also include one or more layers of an oxygen/carbon dioxide/moisture barrier material such as ethylene/vinyl alcohol (EVOH), PEN, polyvinyl alcohol (PVOH), polyvinylidene chloride (PVDC), nylon 6, crystallizable nylon (MXD-6), LCP (liquid crystal polymer), amorphous nylon, polyacrylonitrile (PAN) and styrene acrylonitrile (SAN). The properties of some of these barrier materials are included in the Table of Appendix C at page 49, for comparison purposes.

It may be desirable to use as an oxygen-scavenging catalyst, compounds such as cobalt, manganese, or magnesium with organic ligands. Examples include cobalt neodecanoate, cobalt acetate, magnesium acetate, and manganese acetate. It is believed that the cobalt may reduce the bond energy at the alpha-hydrogen carbonyl site, to provide increased reactivity with oxygen. The organic ligands are believed to promote ingress of the oxygen into the polymer, and facilitate movement of oxidation gases (see Figs. 13A-K).

The intrinsic viscosity (I.V.) effects the processability of the resins. Polyethylene terephthalate having an intrinsic viscosity of about 0.8 is widely used in the carbonated soft drink (CSD) industry. Polyester resins for various applications may range from about 0.55 to about 1.04, and more particularly from about 0.65 to 0.85dl/g. Intrinsic viscosity measurements of polyester resins are made according to the procedure of ASTM-D-2857, by employing  $0.0050 \pm 0.0002$  g/ml of the polymer in a solvent comprising o-chlorophenol (melting point  $0^{\circ}\text{C}$ ), respectively, at  $30^{\circ}\text{C}$ . Intrinsic viscosity (I.V.) is given by the following formula:

$$\text{I.V.} = (\ln(V_{\text{Soln.}}/V_{\text{Sol.}}))/C$$

where:

$V_{\text{Soln.}}$  is the viscosity of the solution in any units;

$V_{\text{Sol.}}$  is the viscosity of the solvent in the same units; and

C is the concentration in grams of polymer per 100 mls of solution.

25

The polymers as used herein (aromatic ester oxygen-scavenging polymer and biaxially-oriented polyester polymer) are high polymers, having a molecular weight of at least about 50,000, for which the melt viscosity is an important process parameter. If the melt viscosity is too high, it is not possible to push the polymer through the injection manifold fast enough to produce commercial preforms. Another important parameter is melt strength; if the melt strength is too low, it is not possible to maintain layer integrity in a multilayer structure having one or more relatively thin layers. Generally, as the molecular weight of the polymer

30

increases, both the melt viscosity and melt strength increase. Those skilled in the art can determine an appropriate combination of melt viscosity and melt strength for the scavenging polymer and the polyester polymer. The melt viscosity is generally represented as a melt index, measured according to ASTM 1238B. For example, Shell 8006 virgin PET has a melt index of 29g/10 minutes. It has been found that an adjacent scavenging layer should preferably have a melt index of from 50-100g/10 minutes.

The blown container body should be substantially transparent. One measure of transparency is the percent haze for transmitted light through the wall ( $H_T$ ) which is given by the following formula:

$$H_T = [Y_d / (Y_d + Y_s)] \times 100$$

where  $Y_d$  is the diffuse light transmitted by the thickness of the specimen, and  $Y_s$  is the specular light transmitted by the thickness of the specimen. The diffuse and specular light transmission values are measured in accordance with ASTM Method D 1003, using any standard color difference meter such as model D25D3P manufactured by Hunterlab, Inc., Reston, Virginia, U.S.A. The container body should have a percent haze (through the panel wall) of less than about 10%, and more preferably less than about 5%.

~~The preform body-forming portion should also be substantially amorphous and transparent, having a percent haze across the wall of no more than about 10%, and more preferably no more than about 5%.~~

The container will have varying levels of crystallinity at various positions along the height of the bottle from the neck finish to the base. The percent crystallinity may be determined according to ASTM 1505 as follows:

$$\% \text{ crystallinity} = [(d_s - d_a) / (d_c - d_a)] \times 100$$

where  $d_s$  = sample density in  $\text{g/cm}^3$ ,  $d_a$  = density of an amorphous polymer of zero percent crystallinity, and  $d_c$  = density of the crystal calculated from unit cell parameters. The panel portion of the container is stretched the greatest and preferably has an average percent crystallinity of at least about 15%, and more preferably at least about 20%. Generally, a 25 to 29% crystallinity range is useful in the panel region.

Further increases in crystallinity can be achieved by heat setting to provide a combination of strain-induced and thermal-induced crystallization. Thermal-induced crystallinity is achieved at low temperatures to preserve transparency, e.g., holding the container



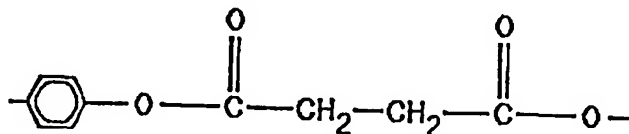
in contact with a low temperature blow mold. In some applications, a high level of crystallinity at the surface of the sidewall alone is sufficient.

The oxygen-scavenging material of this invention may be made by a masterbatch process, wherein the oxygen-scavenging polymer is prepared first, and then blended or  
 5 copolymerized with the PET polymer. A masterbatch process for combining an oxygen-scavenging polymer with PET is described in copending and commonly-owned U.S. Serial No. 08/355,703, filed December 14, 1994, entitled OXYGEN-SCAVENGING COMPOSITIONS FOR MULTILAYER PREFORM AND CONTAINER (docket no. 7180), which was published as WO 96/18685 on June 20, 1996, and is hereby incorporated by reference in its entirety.

10 The average molecular weight of the oxygen-scavenging polymer may be selected, for various purposes. One such purpose is to improve the blendability with the PET polymer, and for this purpose the average molecular weight of the oxygen-scavenging polymer is preferably in the range of 70,000-100,000, and more preferably 78,000-94,000.

The compatibility of the oxygen-scavenging polymer with the PET polymer may  
 15 be determined by preparing and combining (blending or copolymerizing) samples thereof. Alternatively, it may be determined based on various known compatibility indicators. For example, it has been found that REVPET has a solubility parameter, determined according to a known Van Krevelen method, which is substantially identical to that of unmodified PET. There is a commercially-available software program known as Polymer-CAD, Version 1.6, published  
 20 by Novel Advanced Systems For Engineering And Research, P.O. Box 130304, Ann Arbor, Michigan 48113-0304, USA, which allows one to calculate several fundamental properties of a polymer from its structure based on different Additive Group Contribution methods. For example, utilizing the following structure for REVPET:

- 25 ▶ formula:  $C_{10}H_8O_4$
- ▶ molecular weight: 192.170800
- ▶ structure:



30

the cohesive energy and solubility parameter are determined using direct and molar attraction constant contribution methods. A molar volume of  $144.24 \text{ cm}^3/\text{mole}$  is used, at  $298^\circ\text{K}$ . See Van Krevelen, D.W. and Hoftyzer, P.J., J. Appl. Polymer Sci., 13, page 871 (1969); and

Van Krevelen, D.W., Properties Of Polymers, 3rd Edition, Elsevier Science Publishers (1990). The method utilizes the group contribution to the molar volume of the amorphous polymer, followed by that for the crystalline polymer in  $\text{cm}^3/\text{mole}$  (gram basis). This is an aggregation of the data of four methods: two to calculate the Cohesive Energy ( $E_{\text{coh}}$ ) from Bunn, C.W.,  
 5 J.Polymer Sci., 16, page 323 (1955), and Hostyzer, P.J., and Van Krevelen D.W., International Symposium On Macromolecules (IUPAC), Paper No. IIIa-15 (1970); and two to calculate the Attraction Constant (F) from Small, P.A., J.Appl. Chem., 3, page 71 (1953), and Van Krevelen, D.W., Fuel, 44, page 236 (1965). The method of Bunn applies at the boiling point only, while the others apply at 298°K.

10 The solubility parameter (Van Krevelen 1) for REVPET is calculated to be  $20.5283 \text{ J}^{1/2}/\text{cm}^{3/2}$ , using an attraction constant  $F$  (Van Krevelen) =  $2961 (\text{J}\cdot\text{cm}^3)^{1/2}/\text{mole}$  (where  $J$  = Joules and  $\text{cm}$  = centimeters), and a cohesive energy  $E_{\text{coh}}$  (Van Krevelen) =  $60784.3 \text{ J/mole}$ , where solubility parameter =  $(\overline{E_{\text{coh}}}/\text{molar volume})^{1/2}$ , and  $E_{\text{coh}} = F^2/\text{molar volume}$ . The solubility parameter for unmodified PET is the same: 20.5283.

15 Included at the end of the detailed description (before the claims), under the subheading Appendix A, is a sample of the output generated by the Polymer-CAD program for PET having the designated structure. The output includes the: volumetric properties; calorimetric properties; transition temperatures; cohesive energy and solubility; molar refraction and refractive index; electrical properties; magnetic properties; mechanical properties; acoustic  
 20 properties; permachor and permeability; and thermal decomposition temperatures. Similarly, in Appendix B is set forth the sample output for REVPET.

The closer the match of solubility parameters for the oxygen-scavenging polymer and the PET polymer, the more compatible the polymers are expected to be. It is preferred that the polymers have a solubility parameter within 3 units, and more preferably within 1 unit, as  
 25 determined by the above software program (Van Krevelen 1). Included before the claims as Appendix C is a list of the solubility parameters (SOL) and other properties of various polymers. As previously discussed, PET and REVPET have the same value of solubility parameter (20.53). Modified REVPET has a value of 20.18. In contrast, MXD-6 nylon has a much higher value of 26.8, which is well outside the 3 unit preferred range and shows that this polymer is much less  
 30 compatible with PET.

Falling within the preferred range of 3 units are:

REVPET (Fig. 1B);  
modified REVPET (Fig. 1C);  
Distyrene glycol/diphenic acid/glutaric acid (Fig. 1D);  
Bis A Epoxy/Adipic Acid (Fig. 1E);  
5 Styrene Oxide/Adipic Acid (Fig. 1F);  
Bis A Acetate/Adipic Acid (Fig. 1J);  
Bis A Acetate/Suberic Acid (see text re Fig. 1J);  
Styrene Oxide/Succinic Acid (see text re Fig. 1J);  
Distyrene Oxide/Adipic Acid (see text re Fig. 1J);  
10 Distyrene Glycol/Succinic Acid (see text re Fig. 1J); and  
Cyclic Bis A Ester Calprolactone (Fig. 1K).

#### Measurement Of Oxygen-Scavenging

It is a purpose of the present invention to provide an oxygen-scavenging material  
15 which can be used effectively in commercial packaging for food, beverages and other products.  
It is particularly useful in packaging products such as beer, because beer rapidly loses its flavor  
due to oxygen migration. This is also true for products such as citrus products, tomato-based  
products, and aseptically-packaged meat. It is also useful for making carbonated soft drink  
containers. Depending upon the application, a specific scavenging rate may be desirable or  
20 required as discussed hereinafter.

By "oxygen-scavenging rate" it is herein meant to refer to the amount of oxygen a  
packaging structure scavenges in units of nanograms (ng) of oxygen per square centimeter (cm<sup>2</sup>)  
of package surface area, per day (i.e., units of ng/cm<sup>2</sup>/day). Thus, as the surface area of the  
package increases, the scavenging capacity of the package must increase to maintain the same  
25 rate. Also, because beer is more oxygen sensitive than juice, for packages of similar dimensions,  
the oxygen-scavenging rate of a package designed to contain beer should be higher than the  
oxygen-scavenging rate of a package designed to contain fruit juices. The package should have  
an oxygen scavenging rate of at least 5ng/cm<sup>2</sup>/day, and more preferably at least 30ng/cm<sup>2</sup>/day.

A "scavenging performance ratio" as used herein refers to the ratio of the oxygen  
30 permeability of a control package formed of the aromatic polyester only, to the permeability of a  
package including both the polyester and an aromatic ester oxygen-scavenging polymer of this  
invention, where the two packages have the same dimensions. For example, a single-use (e.g., 8-

12 ounce) beer container should have a scavenging performance ratio of at least about 4, and more preferably about 10 or greater. A single-use (e.g., 8-12 ounce) fruit juice container should have a scavenging performance ratio of at least about 1.5, more preferably at least about 4, and most preferably at least about 8.

5                   A package is designed to have a shelf life of several weeks or months. For example, a typical requirement for beer is 1 part per million (ppm) of oxygen over a 112-day shelf life. A one liter bottle can thus have a cumulative 1000 micrograms  $O_2$  over its shelf life (1 ppm = 1 microgram per cubic centimeter (cc) of volume).

                  By way of example, a control container was made from a monolayer of virgin  
10 bottle-grade PET, having a thickness of 13 mils, a diameter of 2.6 inches, and a height of 4.75 inches. The estimated surface area of the container was about 60 inches squared. The container is filled with deoxygenated water. The rate at which oxygen passes from the exterior to the interior of this control container was measured using an oxygen analyzer (model LC700F, Serial No. 695935, available from Mocon Inc., Minneapolis, Minnesota USA), according to ASTM  
15 S1307-90. The oxygen ingress rate for this control bottle was 30,000 ng/package/day. Dividing the oxygen ingress rate by the surface area produces an oxygen ingress rate per square area of 77 ng/cm<sup>2</sup>/day. Generally, one designs a package so that the oxygen-scavenging rate matches the oxygen ingress rate. In this example a container of the same dimensions made from a monolayer of REVPET has an oxygen ingress rate per square area of 1 or less ng/cm<sup>2</sup>/day. In this package,  
20 1 ng/cm<sup>2</sup>/day is equal to 70 ppb of total accumulated oxygen over 112 days. This is a 77 times improvement over the control container.

                  If PEN is used instead of PET, then the control bottle will have an oxygen ingress rate of 6000 ng/package/day, or 18.6 ng/cm<sup>2</sup>/day.

                  If desired, various catalysts may be used to increase the oxygen-scavenging rate  
25 of the oxygen-scavenging material. For example, Eastman 9921 is a PET polymer having residual cobalt; the cobalt acts as a catalyst during preparation of the PET. The residual cobalt has been found to act as a catalyst for oxygen-scavenging when the PET polymer is blended or copolymerized with various oxygen-scavenging compositions. Eastman 9921 is available from Eastman Chemical, Kingsport, Tennessee, USA.

30                   Similarly, the presence of water has been found to enhance the oxygen-scavenging rate. In an expected use of the container for a liquid product containing water, this

enhancement would inherently occur. For example, it has been observed that wet samples will scavenge at a rate as much as 4 times that of dry samples.

### Pasteurization Process

- 5 Prior art pasteurizable carbonated beverage containers are typically made of glass or metal because they can withstand the extended high temperatures and high internal pressures of the pasteurization cycle. Fig. 12 illustrates graphically, as a function of time, the increasing internal temperature and pressure during a known wet process pasteurization cycle for a 16-ounce glass container, which has been filled with a juice product carbonated at 2.5 volumes; "2.5  
10 volumes" means that the volume of carbon dioxide at 0°C under 1 atmosphere is 2.5 times the volume of the liquid. The typical pasteurization cycle, as shown in Fig. 12, includes five steps:
- (1) immersion in bath 1, having a bath temperature of about 43°C, for about 12.5 minutes in order to raise the container and contents up to about the bath-1 temperature;
  - 15 (2) immersion in bath 2, having a bath temperature of about 77°C, for the time from 12.5 to 21 minutes in order to raise the container and contents up to about the bath-2 temperature;
  - (3) immersion in bath 3, having a bath temperature of about 73°C, for the time from 21 to 31.5 minutes in order to hold the container and contents at about the bath-3  
20 temperature;
  - (4) immersion in bath 4, having a bath temperature of about 40°C, for the time from 31.5 to 43 minutes in order to lower the container and contents down to about the bath-4 temperature; and
  - (5) immersion in quench bath 5 for the time from 43 to 60 minutes in order to cool  
25 the container and contents down to about 10°C.

The temperature curve 12 shows that the container and contents remain above 70°C for roughly 10 minutes (in bath 3), during which time the internal pressure increases significantly to about 110 psi ( $1 \times 10^6 \text{ N}\cdot\text{m}^{-2}$ ). This 10-minute hold period at a temperature of about 70 to 75°C provides effective sterilization for most carbonated beverage products, including those  
30 containing 100% fruit juice. A glass container can withstand these temperatures and pressures without deformation.

A plastic container including the oxygen-scavenging polymer of this invention can be made to withstand the temperatures/pressures of pasteurization by one or more of: using a higher  $T_g$  (more thermal resistant) polyester; adjustments to the package design; use of thermal-induced crystallinity; use of crystallized neck finish; etc.

5           While there have been shown and described several embodiments of the present invention, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the scope of the invention as defined by the appending claims.

---

Appendix A

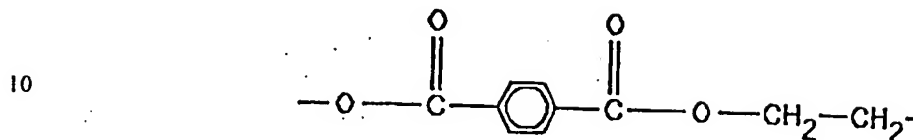
Path:

Name: PET

5 Formula: C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>

Molecular Weight: 192.170800

Structure:

Volumetric Properties:

15

Using Van der Waals Volume Contributions:

Molecular Weight Used: 192.171

V<sub>w</sub>= 94.16 cm<sup>3</sup>/mole

20

V<sub>a</sub>= 1.6 V<sub>w</sub> = 150.656 cm<sup>3</sup>/moleDensity (a)= 1.27556 gm/cm<sup>3</sup>V<sub>c</sub>= 1.435 V<sub>w</sub> = 135.12 cm<sup>3</sup>/mole25 Density (c)= 1.42223 gm/cm<sup>3</sup>

Using Van Krevelen's Molar Volume Contributions:

Molecular Weight Used: 192.171

30 V<sub>a</sub>= 144.24 cm<sup>3</sup>/mole  
Density (a)= 1.3323 gm/cm<sup>3</sup>

35 V<sub>c</sub>= 131.36 cm<sup>3</sup>/mole  
Density (c)= 1.46293 gm/cm<sup>3</sup>

Using Fedors Group Contributions:

Molecular Weight Used: 192.171

5       $V_a = 120.6 \text{ cm}^3/\text{mole}$   
Density (a) = 1.59346 gm/cm<sup>3</sup>

---

Calorimetric Properties:

10    Using Satoh-Shaw Method:

Molecular Weight Used: -192.171

15       $C_{ps} = 1.15262 \text{ J}/(\text{gm K})$   
 $C_{pl} = 1.58141 \text{ J}/(\text{gm K})$

---

Transition Temperatures:

Using Van Krevelen's Glass Transition Temperature Contributions:

20    Molecular Weight Used: 192.171

$$T_g = 350.73 \text{ K}$$

Using Van Krevelen's Crystalline Melting Point Contributions:

25    Molecular Weight Used: 192.171

$$T_m = 566.683 \text{ K}$$

---

Cohesive Energy and Solubility:

30

Using direct & molar attraction constant methods:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

35



	Ecoh (Bunn at Tb)=	46340	J/mole
	Sol. Param. (Bunn at Tb)=	17.924	J <sup>1/2</sup> /cm <sup>3/2</sup>
5	Ecoh (Hoftyzer & Van Krevelen)=	60340	J/mole
	Sol. Param. (Hoftyzer & Van Krevelen)=	20.4531	J <sup>1/2</sup> /cm <sup>3/2</sup>
	F (Small)= 3158 (J.cm <sup>3</sup> ) <sup>(1/2)</sup> /mole		
	Ecoh (Small)= 69141.5 J/mole		
10	Sol. Param. (Small)=	21.8941	J <sup>1/2</sup> /cm <sup>3/2</sup>
	F (Van Krevelen)=	2961	(J.cm <sup>3</sup> ) <sup>(1/2)</sup> /mole
	Ecoh (Van Krevelen)=	60784.3	J/mole
	Sol. Param. (Van Krevelen)=	20.5283	J <sup>1/2</sup> /cm <sup>3/2</sup>
15	Using Fedors Group Contributions:		
	Molecular Weight Used: 192.171		
	Molar Volume Used: 144.24 cm <sup>3</sup> /mole from Van Krevelen 1.		
20	Ecoh (Fedors) =	77820	J/mole
	Sol. Param. (Fedors)=	23.2275	J <sup>1/2</sup> /cm <sup>3/2</sup>
<hr/>			
	Molar Refraction and Refractive Index:		
25	Using Goedhart contributions for several methods:		
	Molecular Weight Used: 192.171		
	Molar Volume Used: 144.24 cm <sup>3</sup> /mole from Van Krevelen 1.		
30	R (Lorentz & Lorenz)=	47.748 cm <sup>3</sup> /mole	
	Refractive Index (Lorentz & Lorenz)=	1.57624	
	R (Gladstone & Dale)= 83.082 cm <sup>3</sup> /mole		
	Refractive Index (Gladstone & Dale)=	1.576	

R (Vogel)= 299.48 gram/mole  
Refractive Index (Vogel)= 1.55841

---

5 Electrical Properties:

Using Van Krevelen contributions for several methods:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

10 P (Lorentz & Lorenz)= 64.3 cm<sup>3</sup>/mole  
Dielectric Constant (Lorentz & Lorenz)= 3.41306  
  
P (Vogel)= 359.88 gram/mole  
Dielectric Constant (Vogel)= 3.50704

15

---

Magnetic Properties:

Using Van Krevelen Diamagnetic Susceptibility Contributions:

20 Molecular Weight Used: 192.171

Molar Diamagnetic Susceptibility= 0.0001015 cm<sup>3</sup>/mole  
Diamagnetic Susceptibility= 5.28176e-007 cm<sup>3</sup>/gm

25

---

Mechanical Properties

Using Rao & Hartmann contributions to Sound Velocity Functions:

30 Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

UR= 8310 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>  
TM= 6450 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>

35

Density= 1.3323 gm/cm<sup>3</sup>

#### Elastic Moduli:

	Bulk	(K)=	4.87185e+010	dync/cm <sup>2</sup>
5	Shear	(G)=	1.06524e+010	dyne/cm <sup>2</sup>
	Tensile	(E)=	2.97861e+010	dync/cm <sup>2</sup>

Poisson Ratio= 0.398101

10

#### Acoustic Properties:

Using Rao & Hartmann contributions to Sound Velocity Functions:

15 Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

UR= 8310 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>

TM= 6450 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>

20

Density= 1.3323 gm/cm<sup>3</sup>

#### Sound Speed:

	Longitudinal (uL)=	2173.2 m/s
25	Shear (uSh)=	894.174 m/s
	Extensional(uext)=	1495.22 m/s

#### 30 Permachor and Permeability:

Using Salame Permachor Method:

Molecular Weight Used: 192.171

Permachor (pi)= 58.8

Permeability of Nitrogen= 7.64892e-016 cm<sup>2</sup>/(s.Pa) at 298K

5

---

Thermal Decomposition Temperatures:

Using Van Krevelen's (1/2) Decomposition Temperature

Contributions:

10 

Molecular Weight Used: 192.171

Td(1/2)= 718.111 K

---

The '\*\*' before a property name indicates missing group values!

15

Appendix B

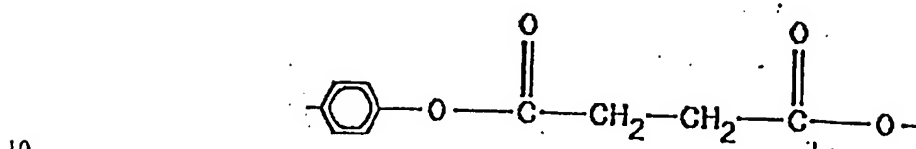
Path: C:\Program Files\PCAD\Plmrl.ecb

Name: REV PET

Formula: C10H8O4

5 Molecular Weight: 192.170800

Structure:

Volumetric Properties:

Using Van der Waals Volume Contributions:

15 Molecular Weight Used: 192.171

vw= 94.16 cm<sup>3</sup>/mole

20 Va= 1.6 Vw = 150.656 cm<sup>3</sup>/mole  
Density (a)= 1.27556 gm/cm<sup>3</sup>

Vc= 1.435Vw 135.12 cm<sup>3</sup>/mole  
Density (c)= 1.42223 gm/cm<sup>3</sup>

25 Using Van Krevelen's Molar Volume Contributions:

Molecular Weight Used: 192.171

30 Va= 144.24 cm<sup>3</sup>/mole  
Density (a)= 1.3323 gm/cm<sup>3</sup>

Vc= 131.36 cm<sup>3</sup>/mole  
Density (c)= 1.46293 gm/cm<sup>3</sup>

Using Fedors Group Contributions:

Molecular Weight Used: 192.171

35

Va= 120.6 cm<sup>3</sup>/mole  
Density(a)= 1.59346 gm/cm<sup>3</sup>

---

5 Calorimetric Properties:

Using Satoh-Shaw Method:

Molecular Weight Used: 192.171

10 Cps= 1.15262 J/ (gm K)  
Cpl= 1.58141 J/(gm K)

---

15 Transition Temperatures:

Using Van Krevelen's Glass Transition Temperature Contributions:

Molecular Weight Used: 192.171

20 Tg= 110.76 F

Using Van Krevelen's Crystalline Melting Point Contributions:

Molecular Weight Used: 192.171

25 Tm= 420.797 F

---

Cohesive Energy and Solubility:

30 Using direct & molar attraction constant methods:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

Ecoh (Bunn at Tb)= 46340 J/mole  
35 Sol. Param. (Bunn at Tb)= 17.924 J<sup>1/2</sup>/cm<sup>3/2</sup>

	Ecoh (Hoftyzer & Van Krevelen)=	60340	J/mole
	Sol. Param. (Hoftyzer & Van Krevelen)=	20.4531	$J^{1/2}/cm^{3/2}$
	F (Small)=	3158	$(J.cm^3)^{(1/2)}/mole$
5	Ecoh (Small)=	69141.5	J/mole
	Sol. Param. (Small)=	21.8941	$J^{-1/2}/cm^{3/2}$
	F (Van Krevelen)=	2961	$(LT.cm^3)^{-(1/2)}/mole$
	Ecoh (Van Krevelen)=	60784.3	J/mole
10	Sol. Param. (Van Krevelen)=	20.5283	$LT^{1/2}/cm^{-3/2}$

Using Fedors Group Contributions:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

15

Ecoh (Fedors) =	77820	J/mole
Sol. Param. (Fedors)=	23.2275	$J^{1/2}/cm^{3/2}$

---

Molar Refraction and Refractive Index:

20

Using Goedhart contributions for several methods:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

	R (Lorentz & Lorenz)=	47.244 cm <sup>3</sup> /mole
25	Refractive Index (Lorentz & Lorenz)=	1.56883

R (Gladstone & Dale)= 82.242 cm<sup>3</sup>/mole

Refractive Index (Gladstone & Dale)= 1.57017

R (Vogel)= 298.88 gram/mole

30

Refractive Index (Vogel)= 1.55528

---

Electrical Properties:

35

Using Van Krevelen contributions for several methods:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

P (Lorentz & Lorenz)= 64.3 cm<sup>3</sup>/mole

Dielectric Constant (Lorentz & Lorenz)= 3.41306

5 P (Vogel)= 359.88 gram/mole

Dielectric Constant (Vogel)= 3.50704

#### 10 Magnetic Properties:

Using Van Krevelen Diamagnetic Susceptibility Contributions:

Molecular Weight Used: 192.171

15 Molar Diamagnetic Susceptibility= 0.0001015 cm<sup>3</sup>/mole

Diamagnetic Susceptibility= 5.28176e-007 cm<sup>3</sup>/gm

#### 20 Mechanical Properties:

Using Rao & Hartmann contributions to Sound Velocity Functions:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen 1.

25

UR= 8310 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>

UH= 6450 (cm<sup>3</sup>/mole)(cm/s)<sup>1/3</sup>

Density= 1.3323 gm/cm<sup>3</sup>

30

Elastic Moduli:

Bulk (K)= 4.87185e+010 dync/cm<sup>2</sup>

Shear (G)= 1.06524e+010 dyne/cm<sup>2</sup>

Tensile (E)= 2.97861e+010 dyne/cm<sup>2</sup>

35

Poisson Ratio= 0.398101



---

Acoustic Properties:

5 Using Rao &amp; Hartmann contributions to Sound Velocity Functions:

Molecular Weight Used: 192.171

Molar Volume Used: 144.24 cm<sup>3</sup>/mole from Van Krevelen I.

10	UR=	8310	(cm <sup>3</sup> /mole)(cm/s) <sup>1/3</sup>
	UH=	6450	(cm <sup>3</sup> /mole)(cm/s) <sup>1/3</sup>

	Density=	1.3323 gm/cm <sup>3</sup>
--	----------	---------------------------

Sound Speed:

	Longitudinal (uL)=	2173.2 m/s
15	Shear (uSh)=	894.174 m/s
	Extensional(uext)=	1495.22 m/s

---

20 Permachor and Permeability:  
Using Salame Permachor Method:

Molecular Weight Used: 192.171

25	Permachor (pi)=	58.8	
	Permeability of Nitrogen=	7.64892e-016	cm <sup>2</sup> /(s.Pa) at 298K

---

30 Thermal Decomposition Temperatures:

Using Van Krevelen's (1/2) Decomposition Temperature

Contributions:

Molecular Weight Used: 192.171

Td(1/2)=

645.597 F

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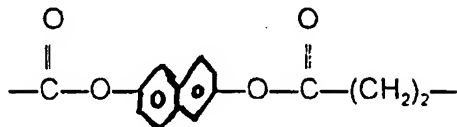
The '\*' before a property name indicates missing group values!

## APPENDIX C

[illegible]

Eg. 1: An example of AROM, CARB and ALPHA weight percentage calculations for REVPEN, molar weight = 242:

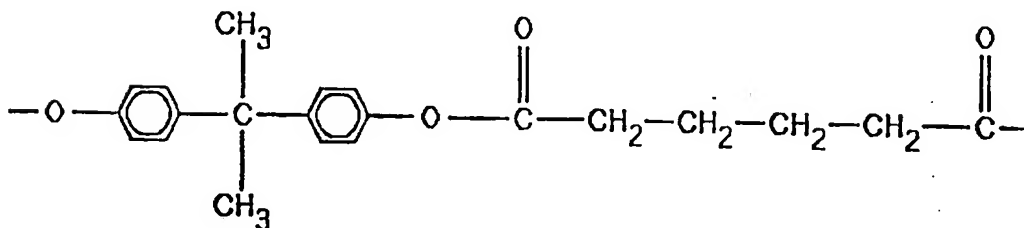
$$\begin{array}{rcl}
 14\text{C} * 12 & = & 168 \\
 10\text{H} * 1 & = & 10 \\
 40 * 16 & = & \underline{64} \\
 & & 242
 \end{array}$$



AROM	$10\text{C} + 6\text{H}$	$= 126/242$	$= 52\%$
CARB	$\text{CO} + \text{CO}$	$= 56/242$	$= 23\%$
ALPHA	$(\text{CH}_2)_2$	$= 28/242$	$= 12\%$

Eg. 2: An example of AROM, CARB and ALPHA weight percentage calculations for polymer 1-J, molar weight = 338:

$$\begin{array}{rcl}
 21\text{C} * 12 & = & 252 \\
 22\text{H} * 1 & = & 22 \\
 40 * 16 & = & \underline{64} \\
 & & = 338
 \end{array}$$



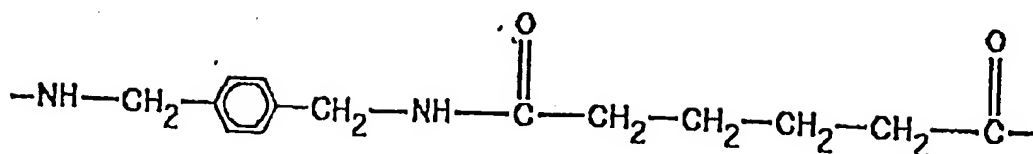
AROM	$\text{C}_6\text{H}_4 + \text{C}_6\text{H}_4 + \text{C}(\text{CH}_3)_2$	$= 194/338$	$= 57\%$
CARB	$\text{CO} + \text{CO}$	$= 56/338$	$= 17\%$
ALPHA	$(\text{CH}_2)_4$	$= 56/338$	$= 17\%$

Eg. 3: An example of AROM, CARB and ALPHA weight percentage calculations for MXD6, molar weight = 246:

$$\begin{array}{rcl}
 {}^{13}\text{C} & * & 12 & = & 156 \\
 {}^1\text{H} & * & 1 & = & 18 \\
 {}^{14}\text{N} & * & 36 & = & \underline{72} \\
 & & & = & 246
 \end{array}$$

5

10



15

AROM  $\text{C}_6\text{H}_4 = 76/246 = 31\%$

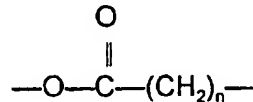
CARB  $\text{CO} + \text{CO} + \text{CO} * .5 + \text{CO} * .5 = 84/246 = 34\%$   
 Note: factor of 1.5 introduced since each CO is next to an NH  
 (see page 13)

20

ALPHA  $(\text{CH}_2)_4 + \text{CH} * .5 + \text{CH} * .5 = 70/246 = 28\%$   
 Note: factor of 1.5 introduced since each CH is next to an NH  
 (see page 13)

## CLAIMS

1. A transparent oxygen-scavenging article comprising:  
 a biaxially-oriented aromatic polyester polymer; and  
 5 an aromatic ester scavenging polymer which includes alpha-hydrogen carbonyl  
 oxygen-scavenging functional groups of the formula:



10 where  $n = 2$  or more, and aromatic groups providing single or multiple aromatic rings in a backbone or side chain of the scavenging polymer;

wherein the scavenging polymer has a glass transition temperature  $T_G$  which  
 15 enables biaxial expansion of both polymers while achieving biaxial orientation of the aromatic polyester in the transparent article.

2. The article of claim 1, wherein the scavenging polymer and aromatic polyester  
 form one or more of a blend, copolymer, and different layers of the article.

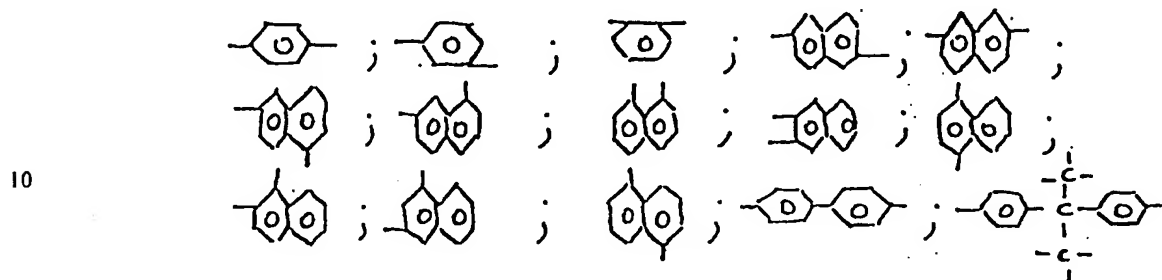
- 20 3. The article of claim 1, wherein the scavenging polymer is selected from the group consisting of homopolymer, random copolymer, alternating copolymer, and block copolymer.

4. The article of claim 1, wherein the aromatic polyester is selected from the group  
 25 consisting of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polypropylene terephthalate, polybutylene terephthalate, polyethylene isophthalate, polycyclohexanedimethanol terephthalate, polypropylene naphthalate, polybutylene naphthalate, polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

- 30 5. The article of claim 4, wherein the aromatic polyester is selected from the group consisting of PET homopolymer and copolymers.

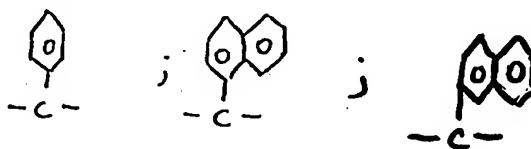
6. The article of claim 4, wherein the aromatic polyester is selected from the group consisting of PEN homopolymer and copolymers.

7. The article of claim 1, wherein the aromatic groups include a backbone ring structure selected from the group consisting of:



and a sidechain ring structure selected from the group consisting of:

15

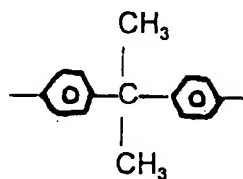


20

8. The article of claim 1, wherein the aromatic groups have one aromatic ring, two aromatic rings, or a double aromatic ring.

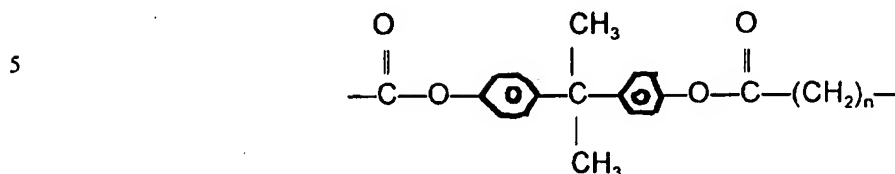
9. The article of claim 1, wherein the aromatic groups are of the formula:

25



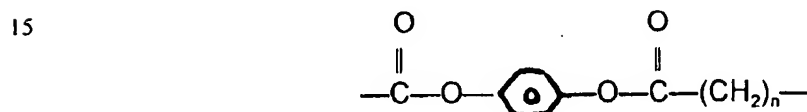
30

10. The article of claim 1, wherein the scavenging polymer has a repeating unit of the formula:



10 were  $n = 2$  or more.

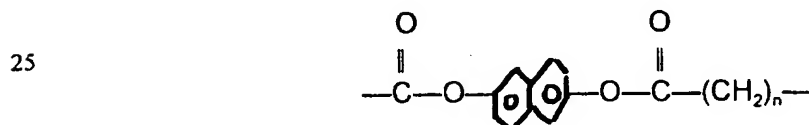
11. The article of claim 1, wherein the scavenging polymer has a REVPET type repeating unit of the formula:



were  $n = 2$  or more.

20

12. The article of claim 1, wherein the scavenging polymer has a REVPEN type repeating unit of the formula:



were  $n = 2$  or more.

30 13. The article of claim 1, wherein the scavenging polymer has a weight percentage of aromatic groups AROM in a range of from 30 to 70.

14. The article of claim 1, wherein the scavenging polymer has a weight percentage of carbonyl groups CARB in a range of from 5 to 30.

35

15. The article of claim 1, wherein the scavenging polymer has a weight percentage of alpha groups ALPHA in a range of from 5 to 30.

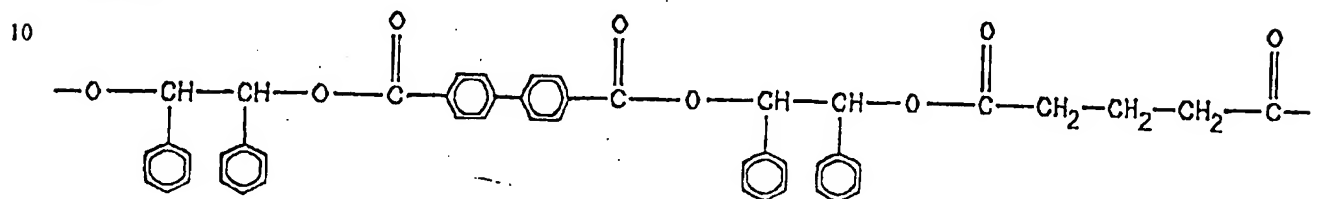


16. The article of claim 1, wherein the scavenging polymer has a repeating unit with one aromatic group, two ester groups, and two alpha-hydrogen carbonyl groups.

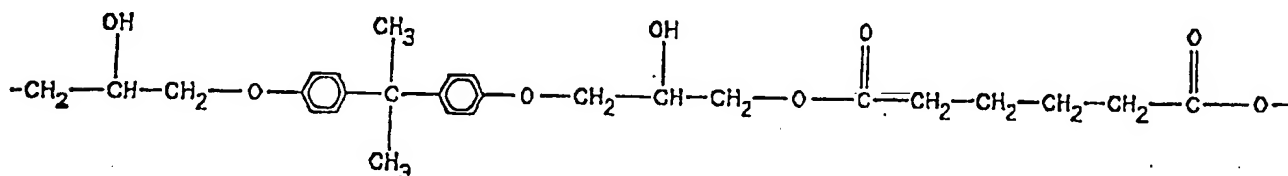
17. The article of claim 16, wherein  $n = 2, 3$  or  $4$ .

18. The article of any one of claims 1, 10, 11, 12 and 16, wherein  $n = 2$ .

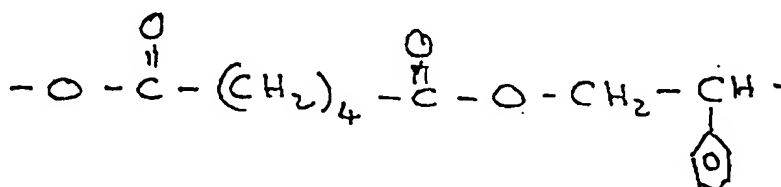
19. The article of claim 1, wherein the scavenging polymer has a repeating unit of the formula:



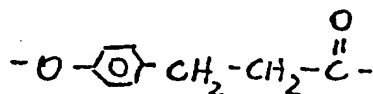
20. The article of claim 1, wherein the scavenging polymer has a repeating unit of the formula:



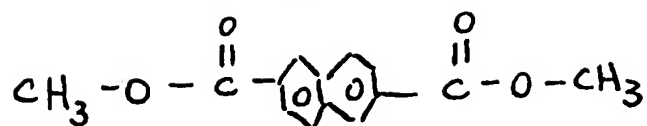
21. The article of claim 1, wherein the scavenging polymer has a repeating unit of the formula:



22. The article of claim 1, wherein the scavenging polymer has a repeating unit of the formula:

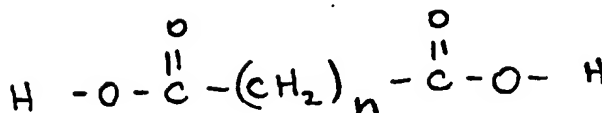


23. The article of claim 1, wherein the scavenging polymer is a random condensation polymer of ethylene glycol with the following 2 components:



5

where n = 2 to 10.



24. The article of claim 1, wherein the scavenging polymer has a Van Krevelen solubility parameter that is within 3 units of the Van Krevelen solubility parameter of the aromatic polyester.

25. The article of claim 24, wherein the Van Krevelen solubility parameter of the scavenging polymer is within 1 unit of that of the aromatic polyester.

26. The article of any one of claims 24 and 25, wherein the Van Krevelen solubility parameter (SOL) is defined by:

$$\text{SOL} = (\text{Ecoh}/\text{molar volume})^{1/2}$$

where Ecoh is cohesive energy defined by  $\text{Ecoh} = F^2/\text{molar volume}$ , and F is a Van Krevelen attraction constant.

27. The article of claim 1, wherein the article has a transparency defined as a percent haze ( $H_T$ ) for transmitted light through a thickness of the article, given by the formula:

$$H_T = [Y_d \div (Y_d + Y_s)] \times 100$$

25

where  $Y_d$  is the diffuse light transmitted by the thickness,  $Y_s$  is the specular light transmitted by the thickness, and the diffuse and specular light transmitted values are measured in accordance with ASTM Method D 1003.

28. The article of claim 27, wherein  $H_T$  is less than 10%.

29. The article of claim 27, wherein  $H_T$  is less than 5%.

30. The article of claim 1, wherein the biaxially-oriented article has an average crystallinity of at least 15% as determined by ASTM 1505 of:

5

$$\% \text{ crystallinity} = [(d_s - d_a)/(d_c - d_a)] \times 100$$

where  $d_s$  = density of article in  $\text{g/cm}^3$ ,  $d_a$  = density of amorphous polymer of zero percent crystallinity, and  $d_c$  = density of crystal calculated from unit cell parameters.

10

31. The article of claim 30, wherein the article has an average crystallinity of at least 20%.

32. The article of claim 1, wherein the scavenging polymer has a  $T_G$  of at least  $10^\circ\text{C}$  below an orientation temperature at which the aromatic polyester undergoes biaxial expansion.

15

33. The article of claim 32, wherein the aromatic polyester is PET and the scavenging polymer has a  $T_G$  of  $70\text{-}85^\circ\text{C}$ .

34. The article of claim 32, wherein the aromatic polyester is PEN and the scavenging polymer has a  $T_G$  of  $120\text{-}135^\circ\text{C}$ .

20

35. The article of claim 1, wherein the scavenging polymer has a crystallization rate no greater than a crystallization rate of the aromatic polyester.

25

36. The article of claim 1, wherein the article is selected from the group consisting of a film, a package, a preform, a blow-molded container, and a portion thereof.

37. The article of claim 36, wherein the article is a wall portion of a pasteurizable, pressurized container.

30

38. The article of claim 1, wherein the article is a package having an oxygen-scavenging rate of at least 5ng/cm<sup>2</sup>/day.

39. The article of claim 1, wherein the article is a package having a scavenging  
5 performance ratio of at least 1.5.

40. The article of claim 1, wherein the article is a package having a scavenging performance ratio of at least 4.

10 41. The article of claim 1, wherein the article is a package having a scavenging performance ratio of at least 8.

42. The article of claim 1, wherein the article is a package having a scavenging performance ratio of at least 20.

15

43. The article of claim 1, wherein the article is a package having a scavenging performance ratio of at least 40.

44. The article of claim 1, wherein the article is a wall portion of a blow molded  
20 container having:

an oxygen-scavenging rate of at least 5ng/cm<sup>2</sup>/day;

an average biaxial stretch ratio of from 9:1 to 15:1; and

at least one layer of the scavenging polymer and at least one layer of the aromatic polyester polymer selected from the group consisting of PET, PEN, and copolymers and  
25 blends thereof.

45. The article of claim 1, wherein the scavenging polymer has a molecular weight of at least 50,000 and a T<sub>G</sub> in a range of from 70 to 135°C.

30

46. A transparent oxygen-scavenging packaging material for holding an oxygen-sensitive product, the material including a biaxially-oriented aromatic polyester polymer and an aromatic ester scavenging polymer, the scavenging polymer including aromatic groups and alpha-hydrogen carbonyl oxygen-scavenging functional groups, the material including one or  
5 more of a blend, copolymer or layer structure of the polyester polymer and the scavenging polymer and having a scavenging performance ratio of at least 10, wherein the ratio is defined as the oxygen permeability of a control material made from the polyester polymer only, to the oxygen permeability of the oxygen-packaging material made from both the polyester polymer and the scavenging polymer.
- 10
47. A transparent oxygen-scavenging package for holding an oxygen-sensitive product, the package including a biaxially-oriented aromatic polyester polymer and an aromatic ester scavenging polymer, the scavenging polymer including aromatic groups and alpha-hydrogen carbonyl oxygen-scavenging functional groups, the material including one or more of a  
15 blend, copolymer or layer structure of the polyester polymer and scavenging polymer and the package having an oxygen-scavenging rate of at least  $5\text{ng}/\text{cm}^2/\text{day}$ .
48. A transparent oxygen-scavenging package for holding an oxygen-sensitive product, the package including a biaxially-oriented aromatic polyester polymer and an aromatic  
20 ester scavenging polymer, the scavenging polymer including aromatic groups and alpha-hydrogen carbonyl oxygen-scavenging functional groups, the material including one or more of a blend, copolymer or layer structure of the polyester polymer and scavenging polymer and the package having a shelf-life of one part per million of oxygen over a period of 112 days.
- 25
49. A container having a transparent multilayer wall formed by biaxial expansion, the multilayer wall including:
- a core layer of an oxygen-scavenging material;
  - inner and outer intermediate layers of an oxygen barrier material; and
  - inner and outer layers of a biaxially-oriented aromatic polyester polymer;
- 30

wherein the oxygen-scavenging layer is adapted to undergo biaxial expansion with the polyester polymer layers and remain transparent while providing an oxygen-scavenging rate of at least 5ng/cm<sup>2</sup>/day.

5            50.            The packaging material or container of any one of claims 46-49, wherein the aromatic polyester is selected from the group consisting of PET, PEN and copolymers and blends thereof.

51. A method of making a transparent oxygen-scavenging article comprising:  
10 providing an aromatic polyester polymer;  
providing an aromatic ester scavenging polymer which includes alpha-hydrogen  
carbonyl oxygen-scavenging functional groups of the formula:

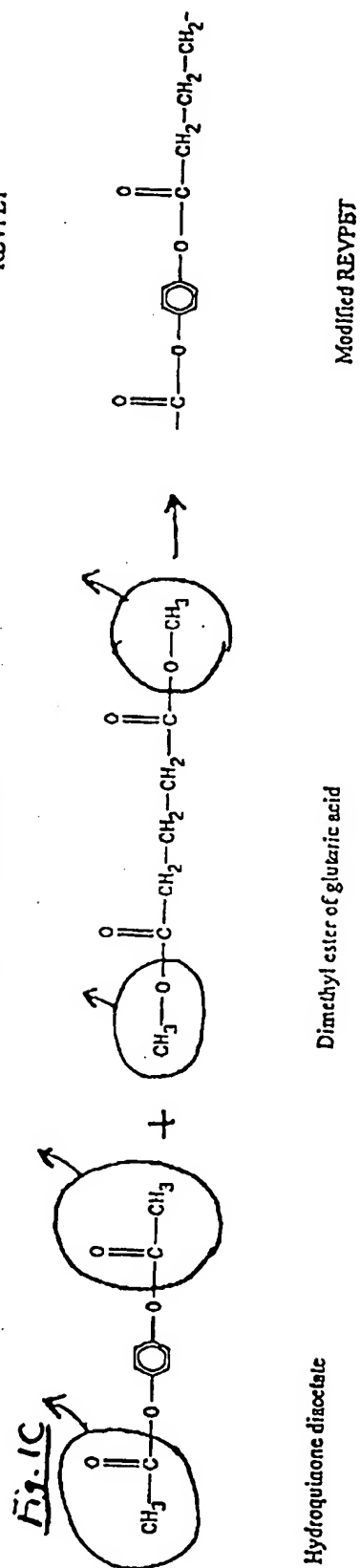
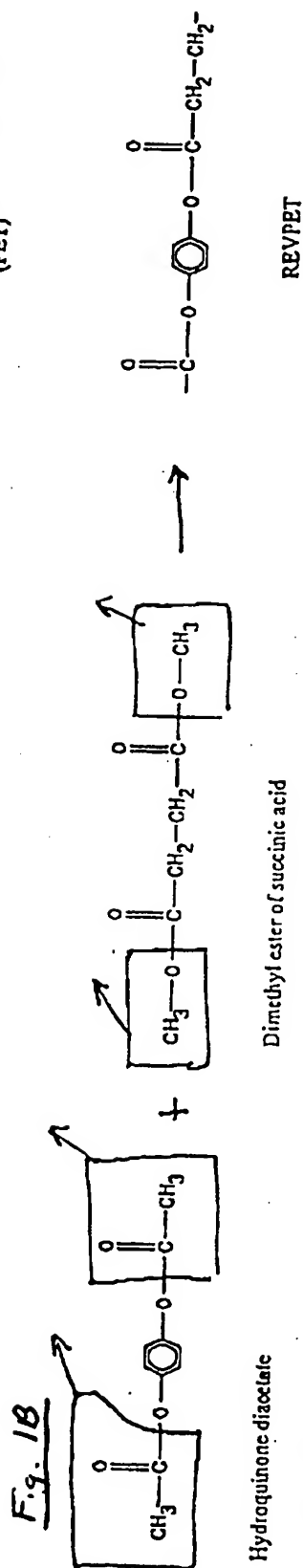
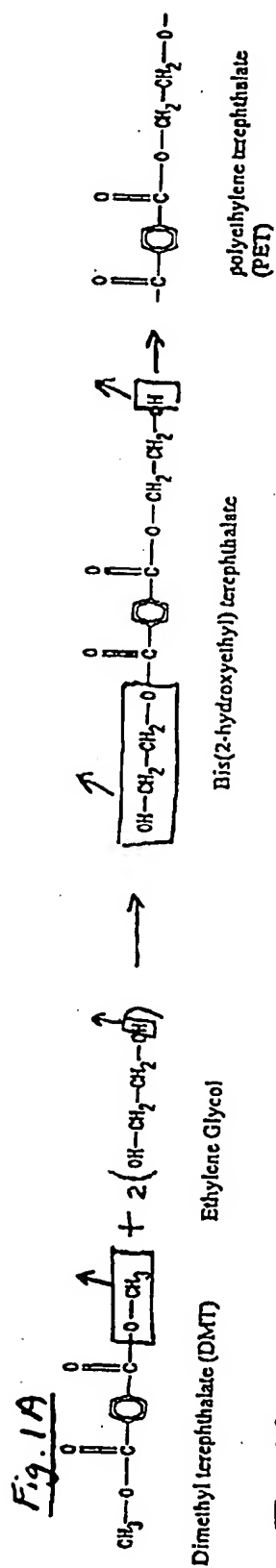


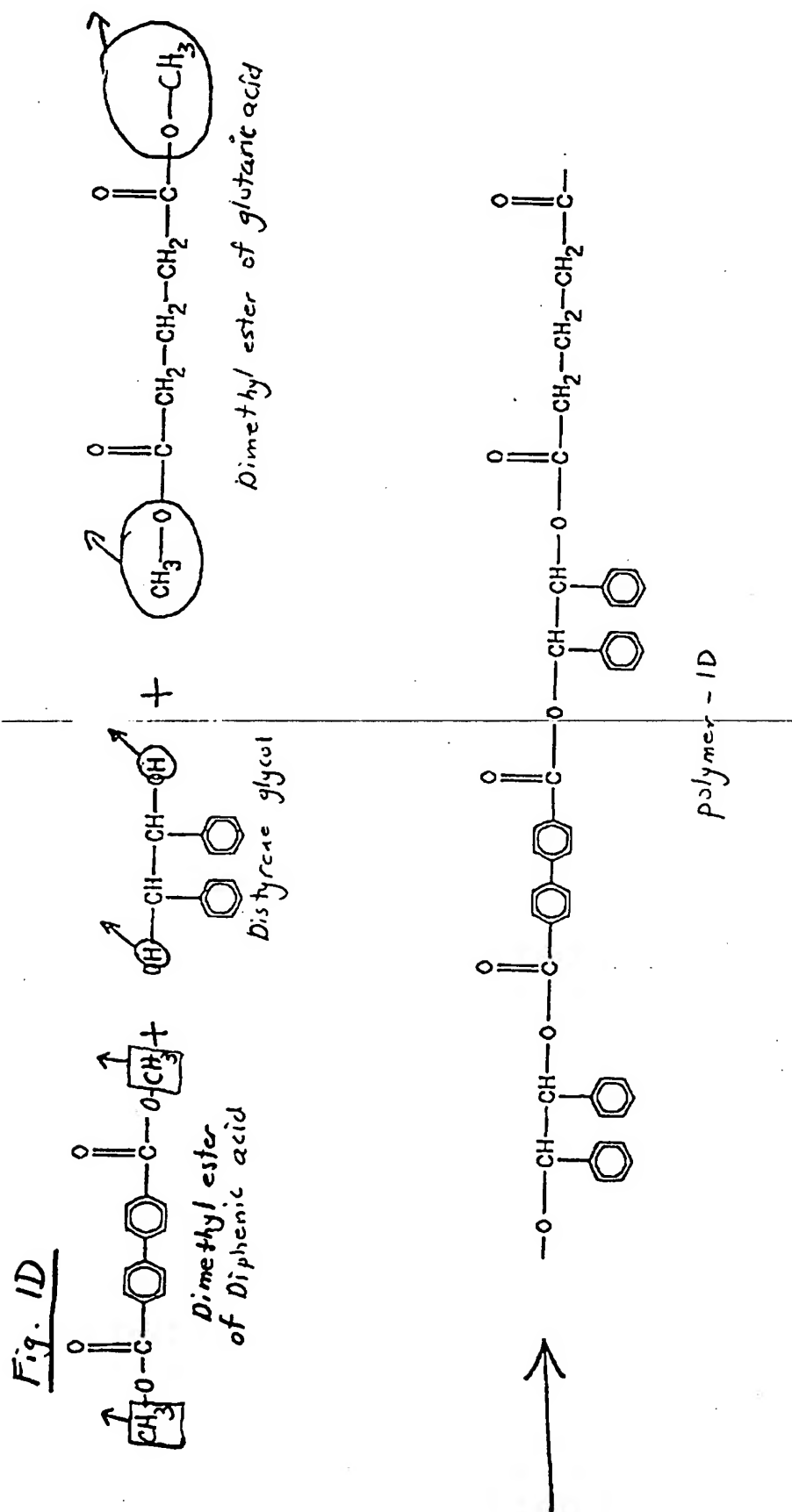
--- where n = 2 or more, and aromatic groups providing single or multiple aromatic rings in a backbone or side chain of the scavenging polymer;

the weight percentages of alpha-hydrogen carbonyl and aromatic groups being selected to adjust a glass transition temperature of the scavenging polymer; and

biaxially expanding the scavenging polymer and the polyester polymer in order to biaxially orient the polyester polymer and form the transparent article.

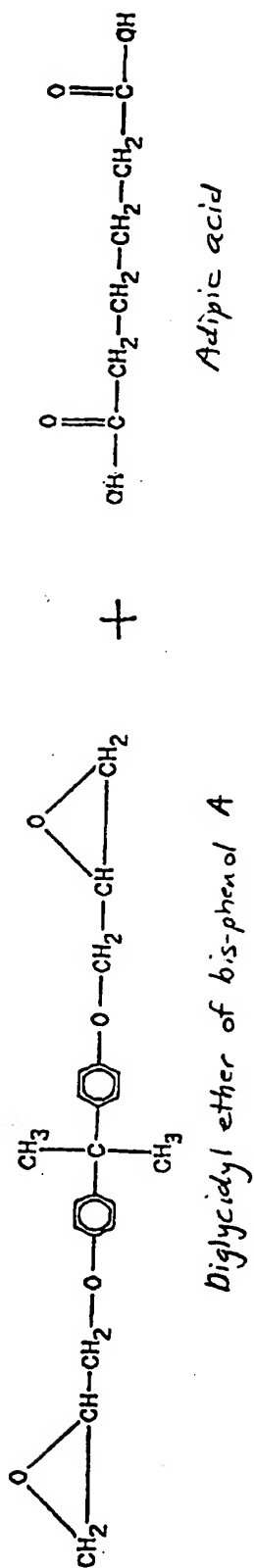
25      52.      The article of claim 32, wherein the aromatic polyester is PEN and the scavenging polymer is amorphous and has a T<sub>G</sub> of 90-100°C.



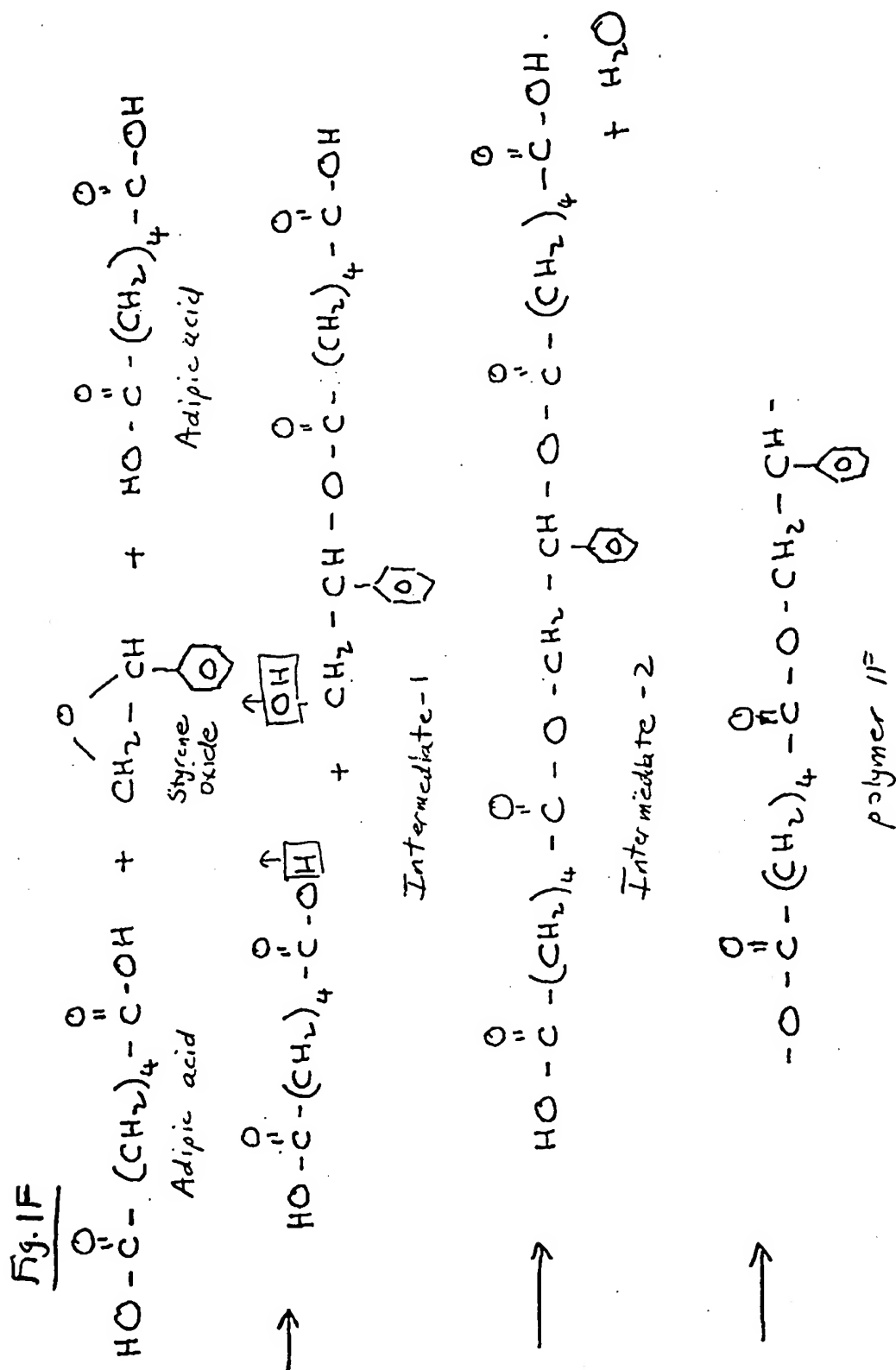




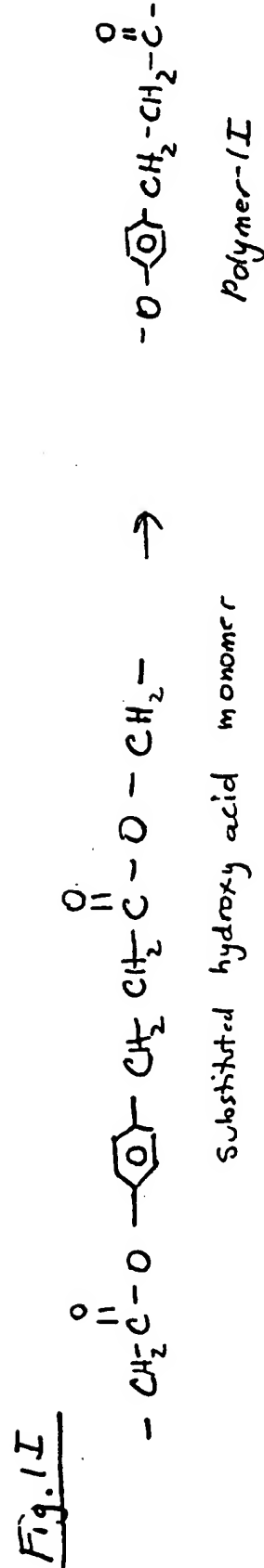
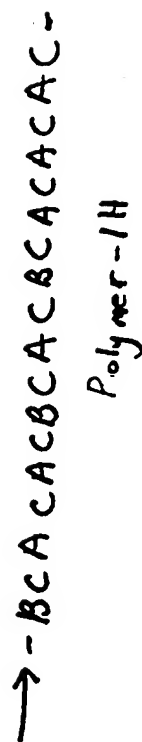
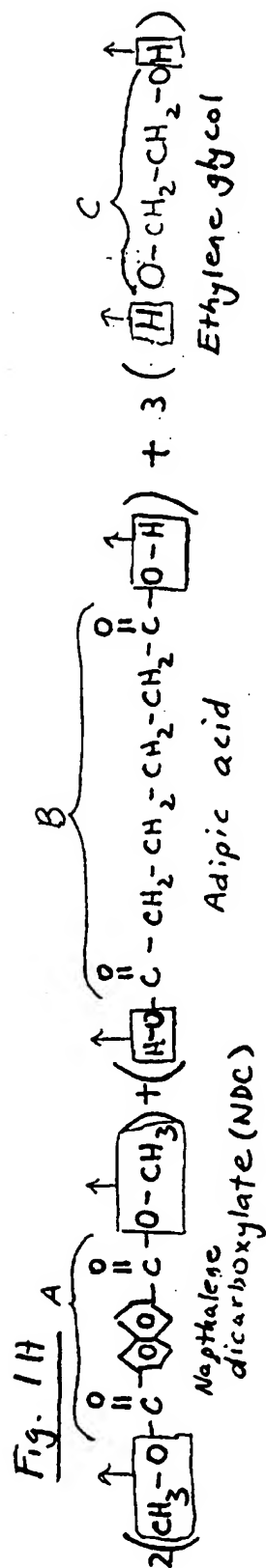
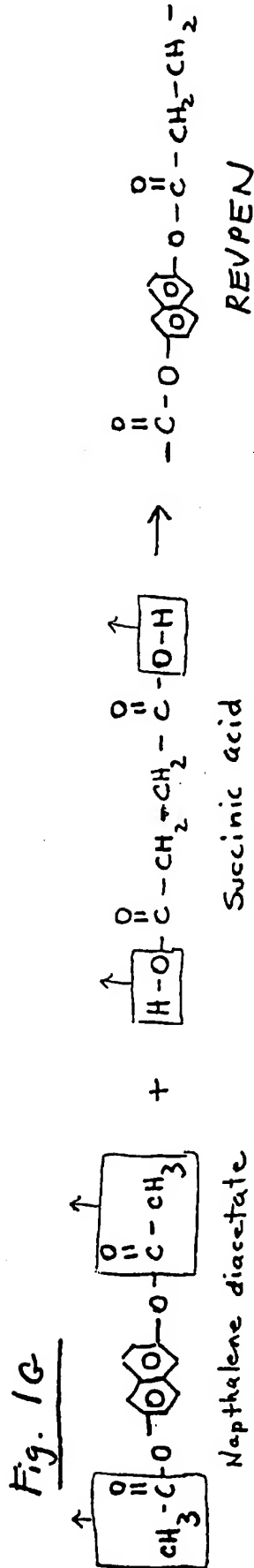
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Fig. 1E

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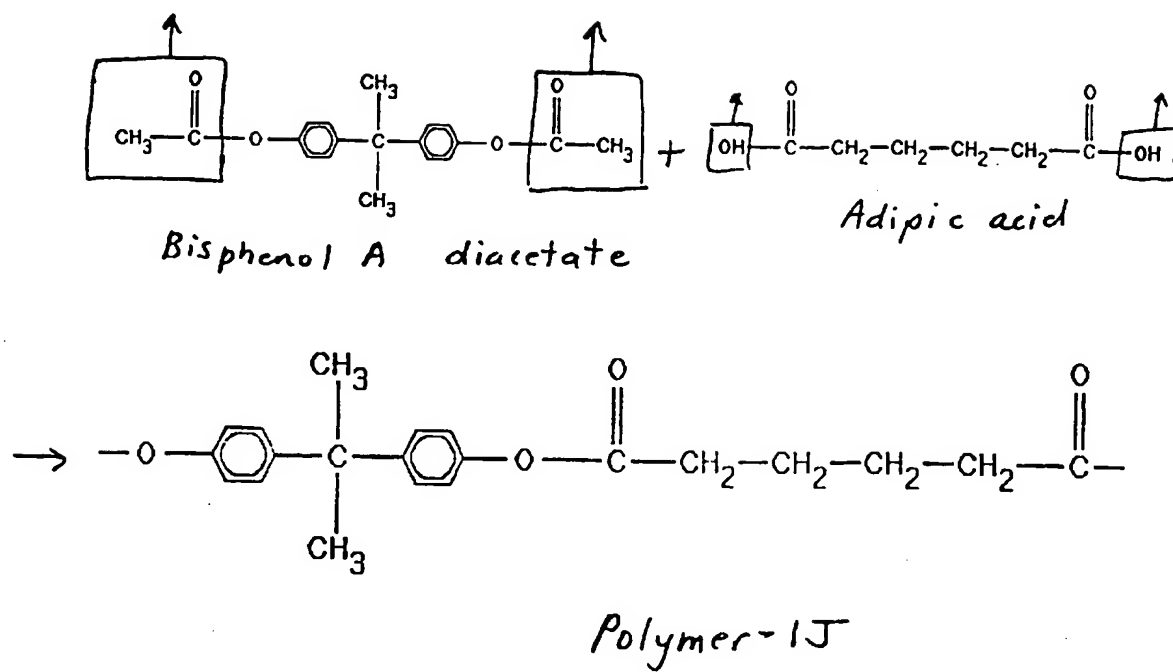
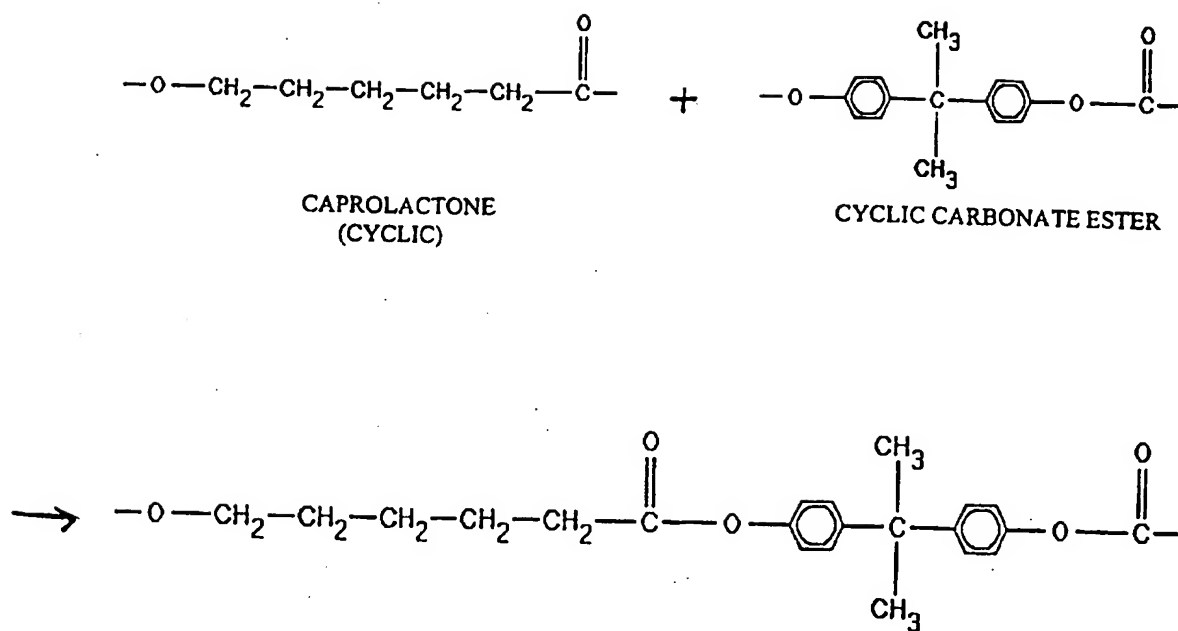
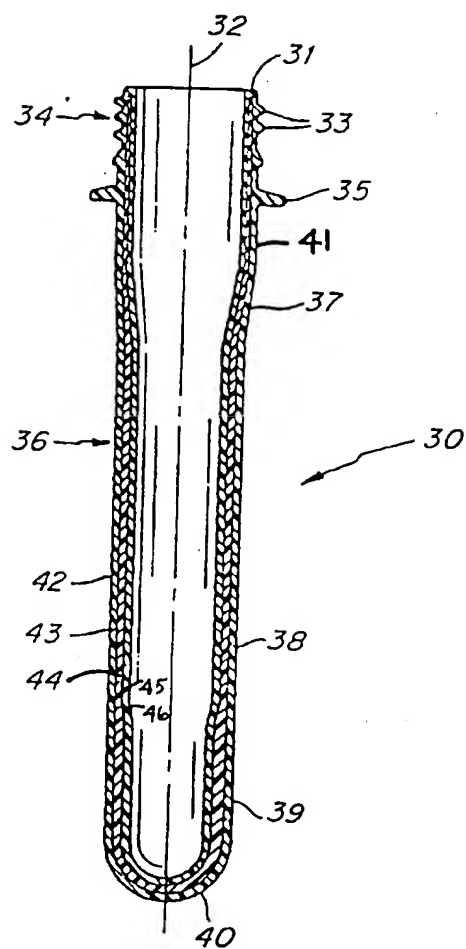


Fig 1J

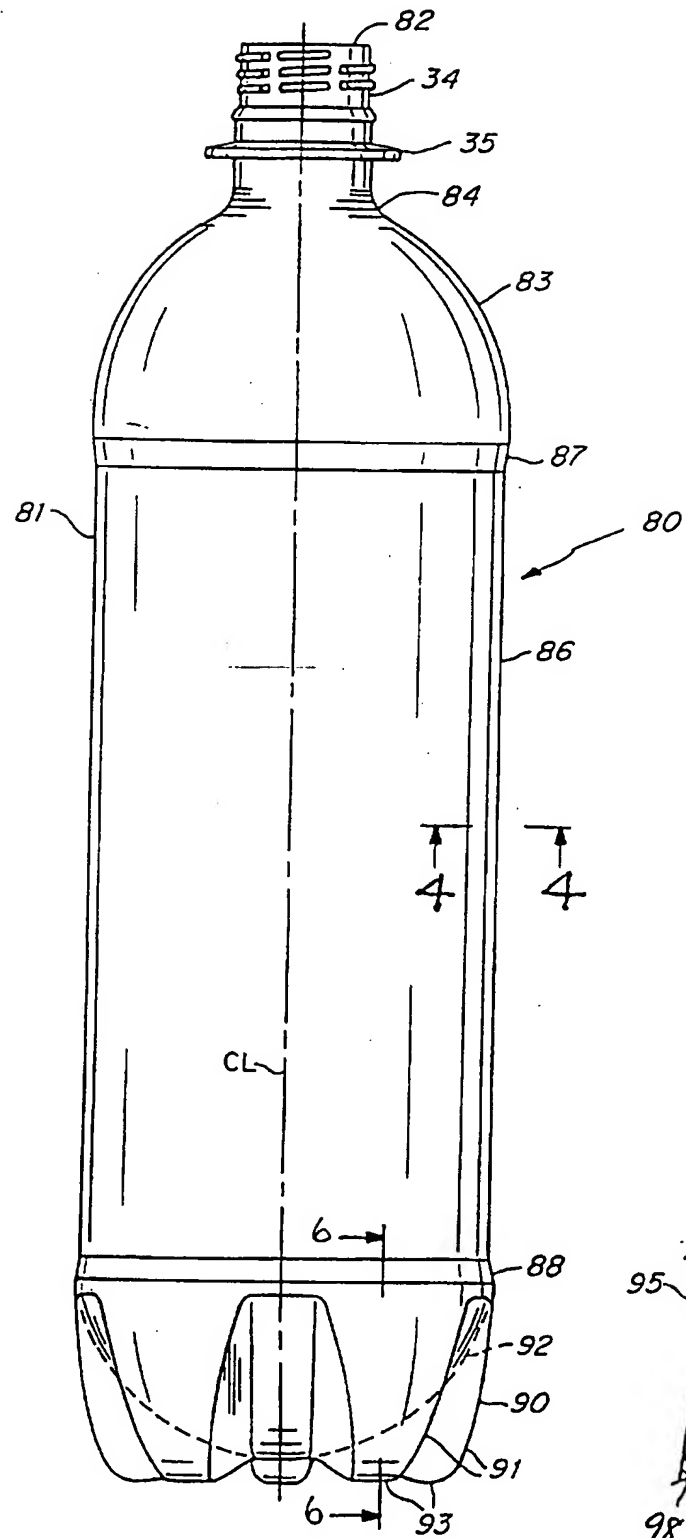
7/20

*Polymer - 1K**Fig. 1K*

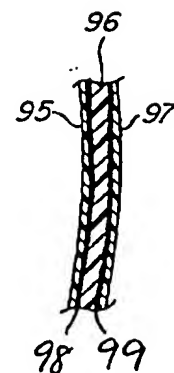
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*Fig. 2*

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*Fig. 3*



*Fig. 4*

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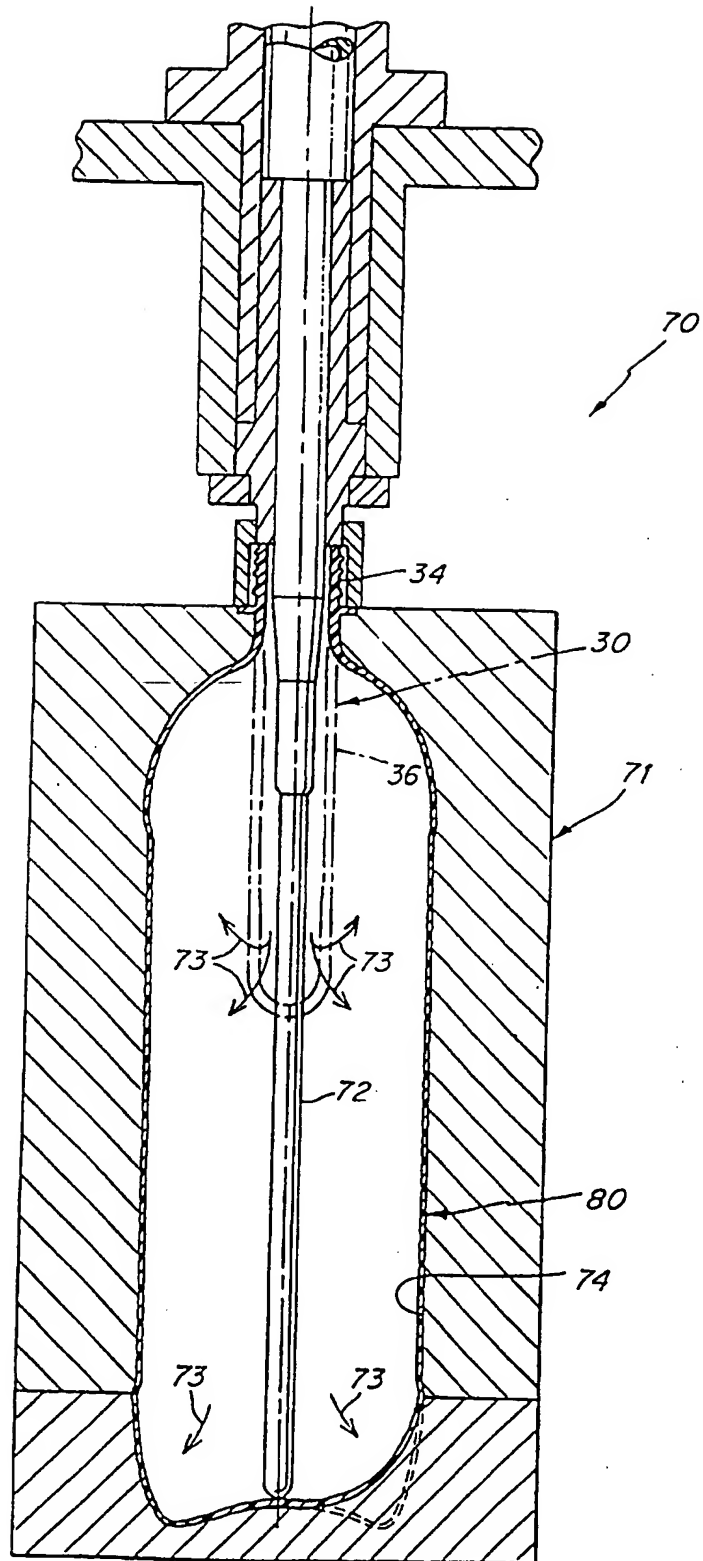
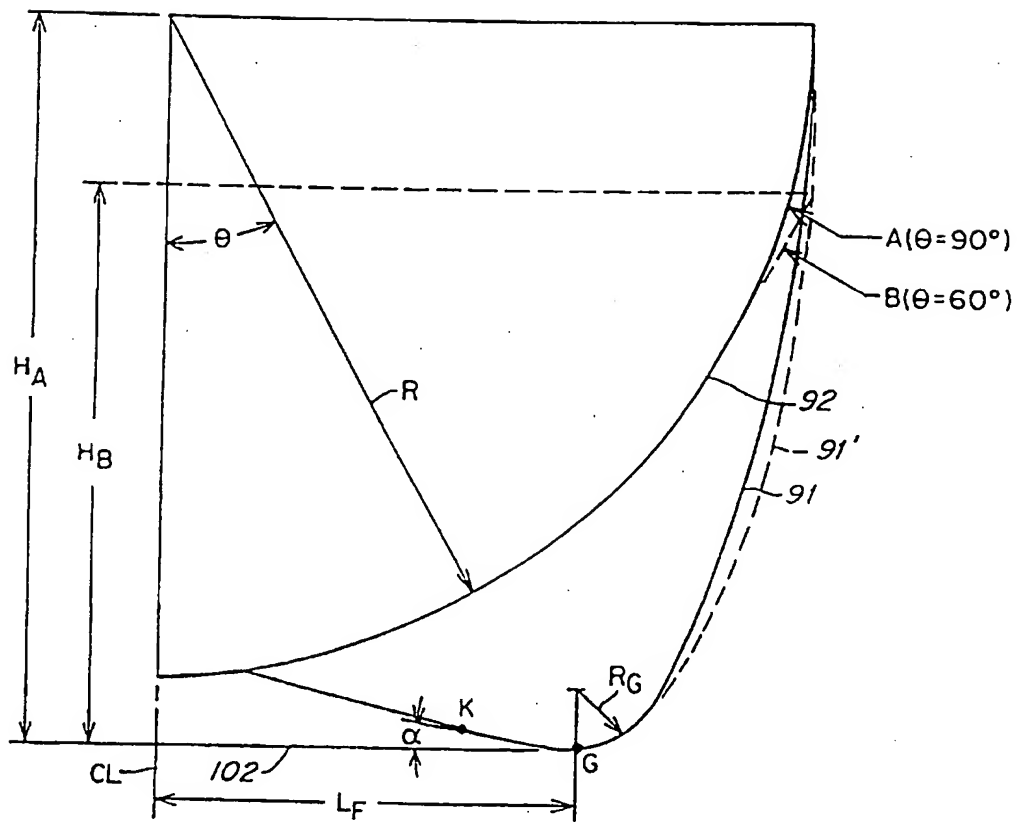


Fig. 5



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*Fig. 6*

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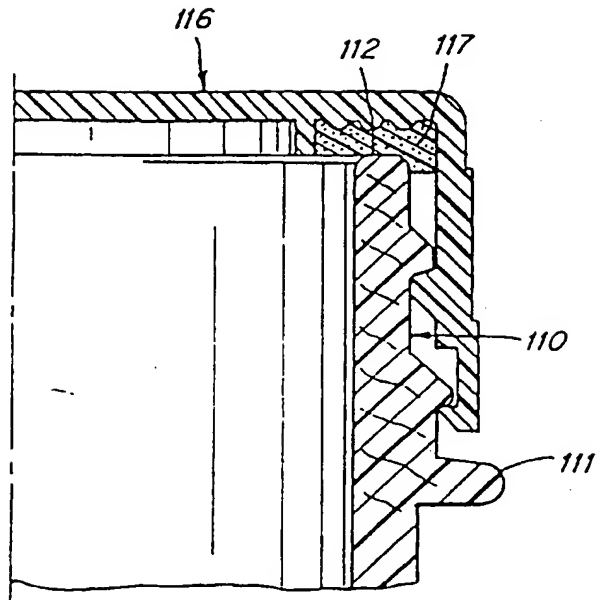


Fig. 7A

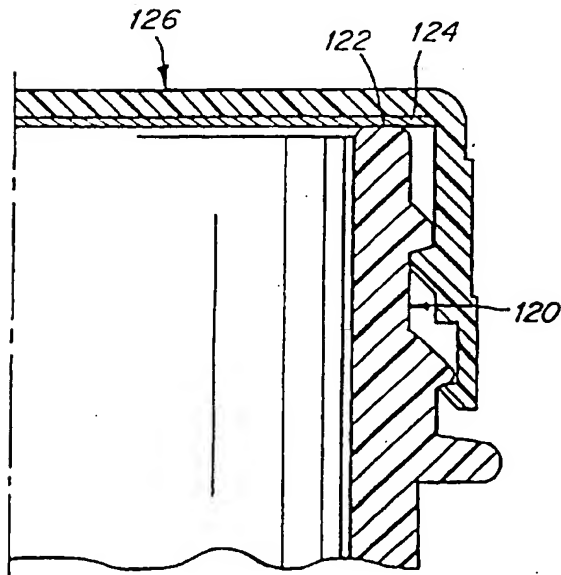
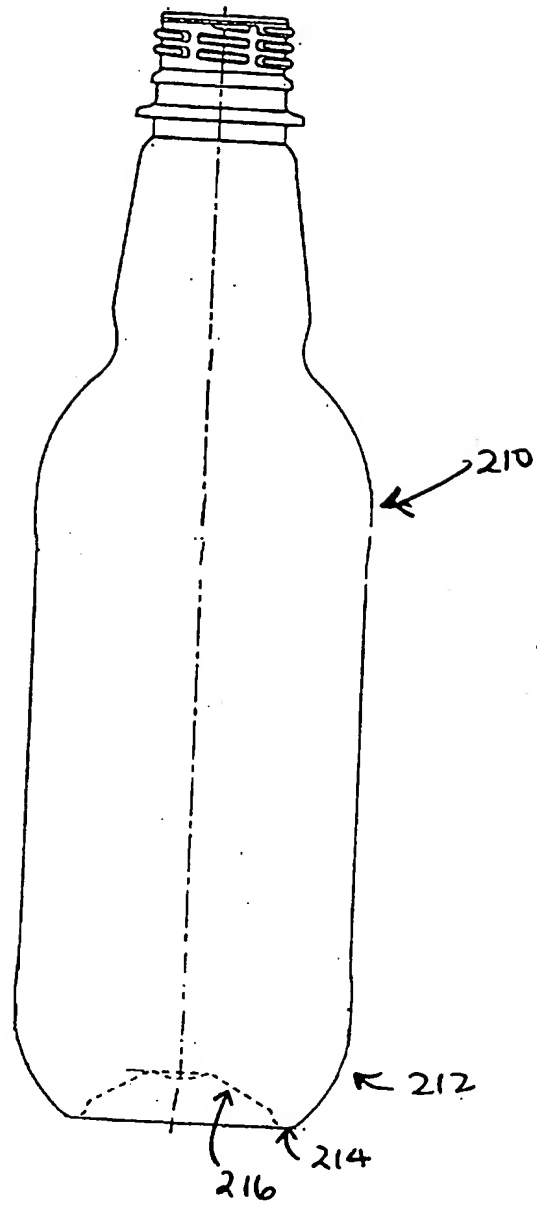
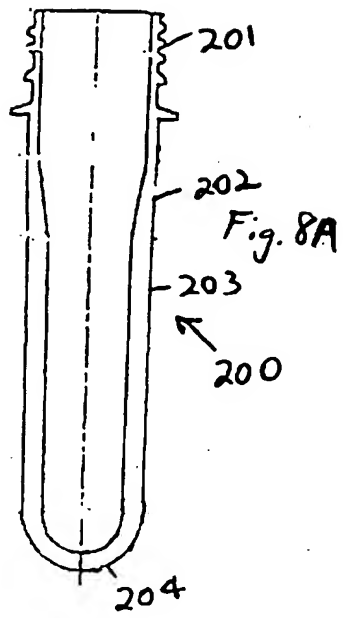


Fig. 7B

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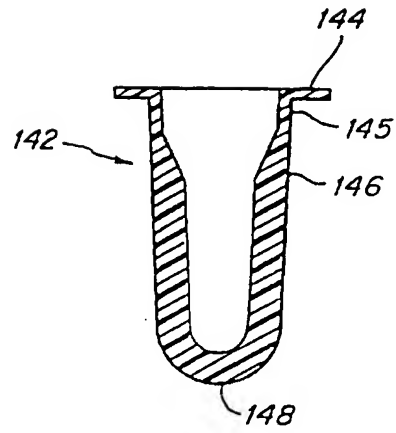


Fig. 9

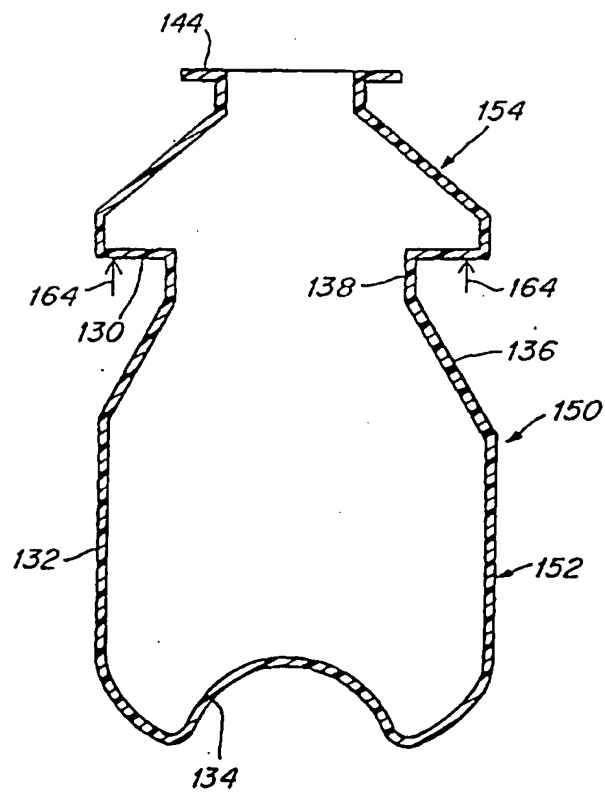
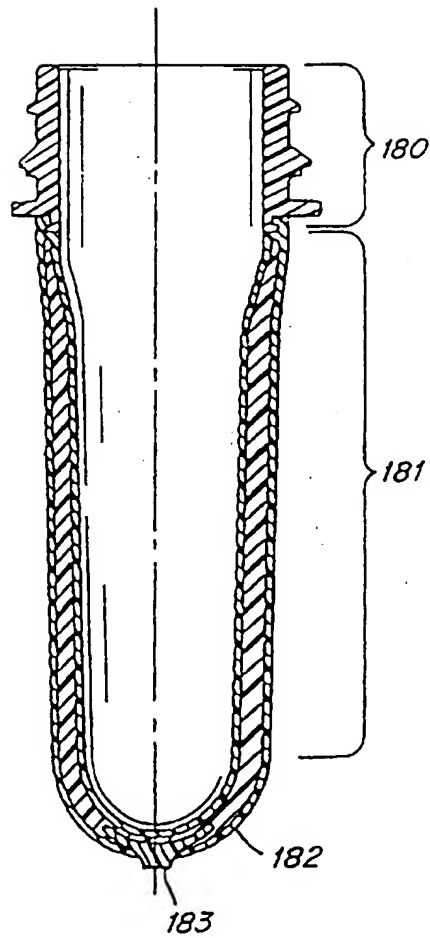
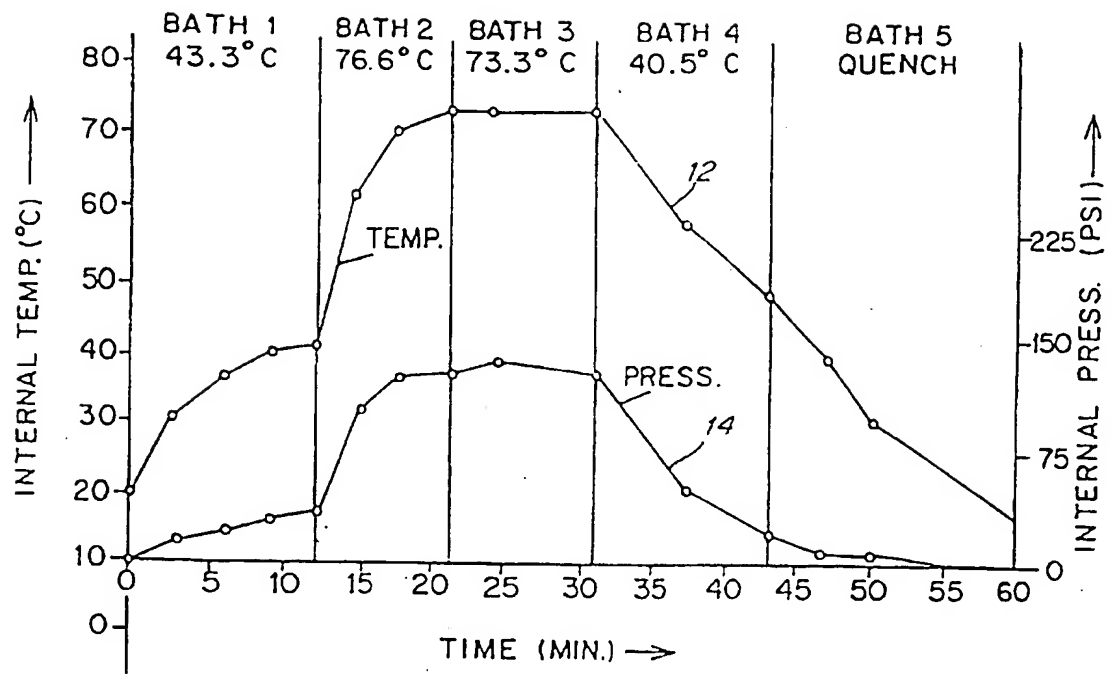


Fig. 10

*Fig.11*

*Fig. 12*

(PRIOR ART)

FIGURE 13A

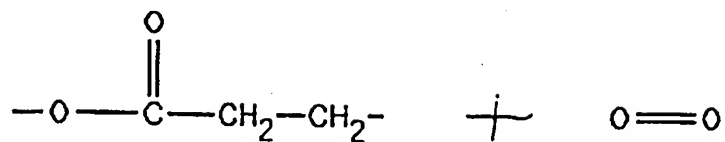


FIGURE 13B



FIGURE 13C

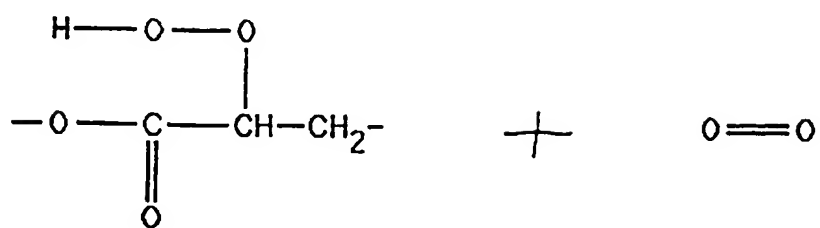
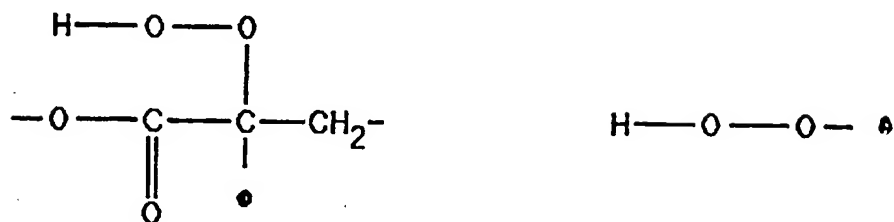


FIGURE 13D



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FIGURE 13E

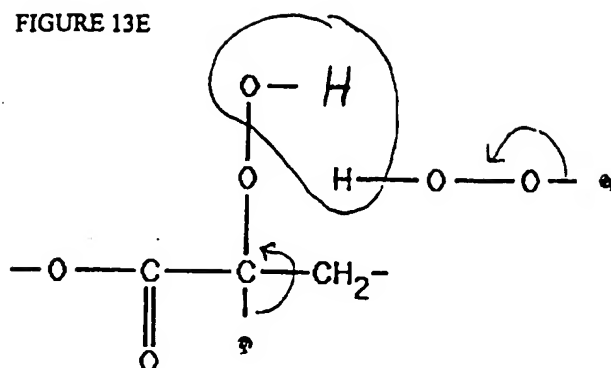


FIGURE 13F

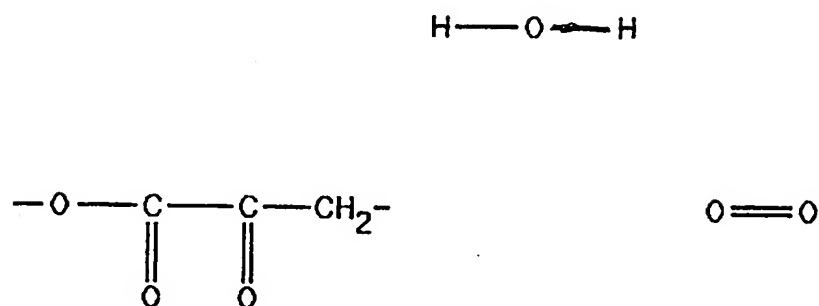


FIGURE 13G

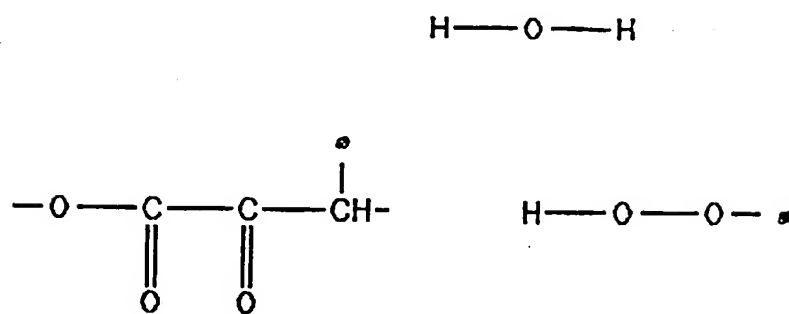




FIGURE 13H

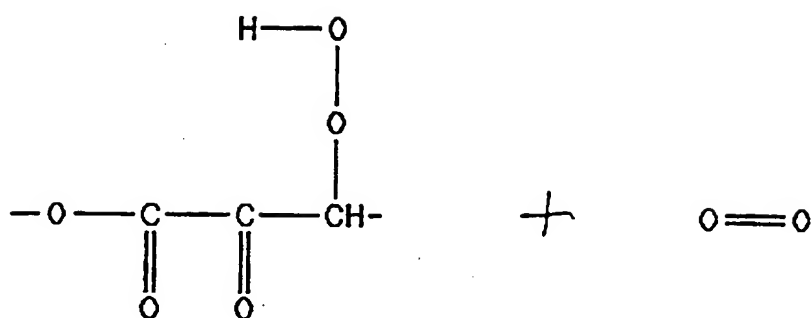


FIGURE 13I

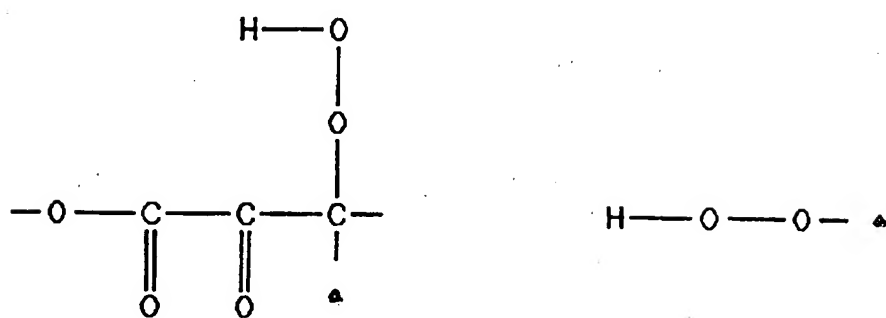
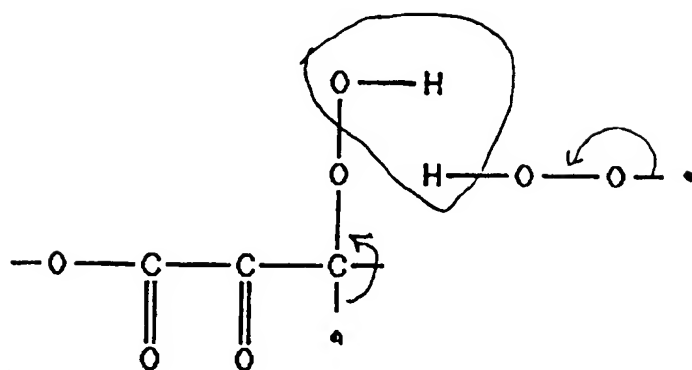
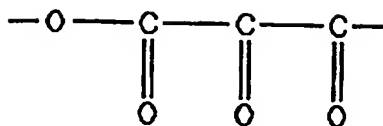
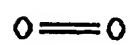
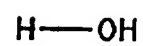


FIGURE 13J



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Fig. 13K



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/16826

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B65D1/00 B65D81/24 B32B27/36 C08G63/18 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B65D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 394 751 A (MITSUI PETROCHEMICAL IND) 31 October 1990  see claims 3-22 see page 3, line 18 - line 32 see page 18, line 29 - page 21, line 12 see examples 102-106, 126 see examples 127, 133-139 see examples 143, 155; table 9 ---	1-8, 18, 32, 33, 36, 45, 51
X	CHEMICAL ABSTRACTS, vol. 118, no. 4, 25 January 1993 Columbus, Ohio, US; abstract no. 23225, XP002051090 see abstract & JP 04 168 148 A (MITSUI PETROCHEMICAL IND.) 16 June 1992 ---	1-5, 7, 8, 23, 36, 51
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PCT/US 97/16826

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 506 014 A (MINNICK, LARRY A.) 9 April 1996 see claims 1-10,18; examples 1-5 see column 2, line 47 - line 62 ---	1-5,7,8, 36,51
Y	US 4 401 805 A (WEEMES, DOYLE A. ET AL) 30 August 1983  see the whole document ---	1-5,7,8, 18,32, 33,36, 37,51
Y	WO 96 18685 A (CONTINENTAL PET TECHNOLOGIES) 20 June 1996 cited in the application  see claims 1-42 see page 13, line 26 - page 15, line 27 ---	1-5,7,8, 18,32, 33,36, 37,51
A	WO 96 18686 A (CONTINENTAL PET TECHNOLOGIES) 20 June 1996  see claims 1-35 see page 11, line 6 - page 17, line 15 ---	1-5, 27-31, 36,37, 44,49-51
A	CHEMICAL ABSTRACTS, vol. 107, no. 10, 7 September 1987 Columbus, Ohio, US; abstract no. 78465, XP002051091 see abstract & JP 62 015 222 A (MITSUI PETROCHEMICAL IND.) 23 January 1987 ---	1-5,7,8, 18,20,36
A	W.M. EARECKSON, III: JOURNAL OF POLYMER SCIENCE, vol. 40, 1959, pages 399-406, XP002051089 cited in the application see page 399 - page 400 -----	1,7-11, 16-18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/16826

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0394751 A	31-10-90	JP 2269116 A	02-11-90
		JP 2641293 B	13-08-97
		JP 2269151 A	02-11-90
		JP 2266938 A	31-10-90
		JP 2269117 A	02-11-90
		JP 2269152 A	02-11-90
		JP 2266939 A	31-10-90
		CA 2014280 A	10-10-90
		CN 1046340 A	24-10-90
-----			
US 5506014 A	09-04-96	WO 9709366 A	13-03-97
-----			
US 4401805 A	30-08-83	NONE	
-----			
WO 9618685 A	20-06-96	AU 4377996 A	03-07-96
		AU 4466996 A	03-07-96
		CA 2207680 A	20-06-96
		CA 2207825 A	20-06-96
		EP 0797627 A	01-10-97
		EP 0797628 A	01-10-97
		WO 9618686 A	20-06-96
-----			
WO 9618686 A	20-06-96	AU 4377996 A	03-07-96
		AU 4466996 A	03-07-96
		CA 2207680 A	20-06-96
		CA 2207825 A	20-06-96
		EP 0797627 A	01-10-97
		EP 0797628 A	01-10-97
		WO 9618685 A	20-06-96
-----			

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